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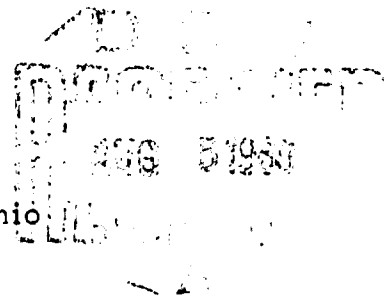
IMPROVED CVD BORON FILAMENT PRODUCTION

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General Electric Company

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Air Force Materials Laboratory  
Air Systems Command  
Wright-Patterson Air Force Base, Ohio



## FOREWORD

This Final Technical Documentary Report was compiled and edited by L. R. McCreight, Program Manager, from reports prepared by the engineers and scientists in the Space Sciences Laboratory of the General Electric Company, working on each of the five tasks in the first phase of the program. This work was performed under Air Force Contract F33615-67-C-1478, Project 364-7, which was administered under the direction of the Chemical Processing Branch of the Manufacturing Technology Division of the Air Force Materials Laboratory by Mr. Gail E. Eichelman. The manuscript was released by the authors 11 June 1968 for publication.

The work described was performed during the thirteen month Phase I period of the program, from 15 March 1967 to 30 April 1967, and was for development of an advanced, integrated, manufacturing production unit for CVD preparation of boron-on-glass filaments. The effort was carried out in five tasks performed by the following principal personnel: Dr. E. C. Henry, Dr. J. J. Gebhardt, Mr. M. J. Arnoff, Mr. B. Gorowitz, Dr. R. B. Reeves, Mr. V. J. Mazzio, Mr. A. L. Speece and Mr. W. J. Reiley.

The project has been accomplished as a part of the Air Force Manufacturing Methods Program, the primary objective of which is to develop, on a timely basis, manufacturing processes, techniques and equipment for use in economical production of USAF materials and components. The program encompasses the following technical areas:

Chemical - Propellant, Coating, Ceramics, Graphite, Nonmetallics  
Electronic - Solid State, Materials & Special Techniques, Thermionics  
Fabrication - Forming, Material Removal, Joining, Components  
Metallurgy - Rolling, Forging, Extruding, Casting, Fiber, Powder

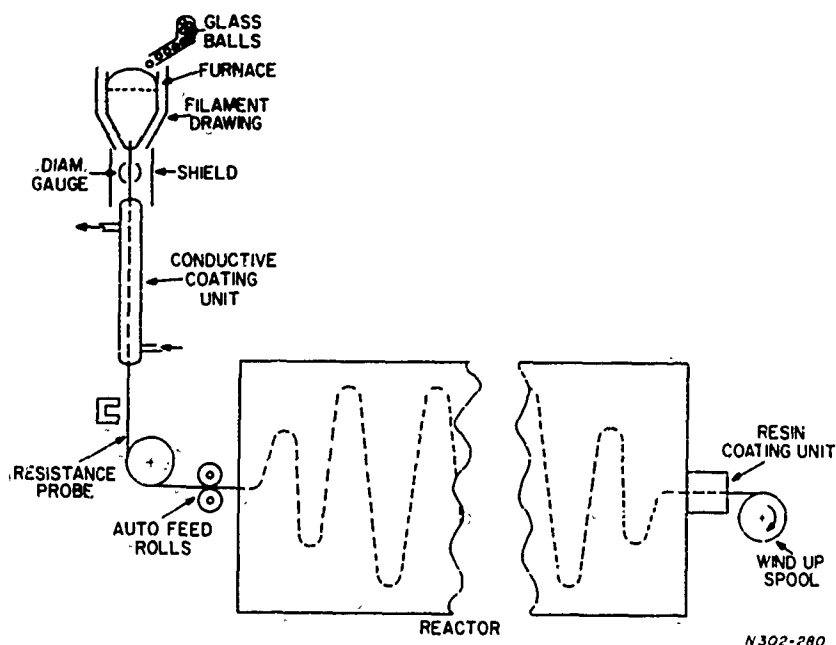
This technical report has been reviewed and is approved.



FRANK J. HARSACKY, Acting Chief  
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## ABSTRACT

The feasibility of producing CVD Boron filaments using diborane and carbon-coated fused silica (glass) having valuable specific mechanical properties has been previously demonstrated. In addition, it was estimated that this type of boron filament can be produced economically in large quantities (\$25-\$50 per pound in a million pound per year plant). Major improvement in the economics of boron filament production were postulated to be achievable by using an even lower cost glass core and by integrating the entire sequence of processes into an in-line process operating at high speed as depicted in the accompanying sketch. The purpose of the work reported here was to develop



and demonstrate the individual manufacturing processes which could then be integrated together in the next program. A brief description of the work performed on the tasks follows:

(1) In-line glass monofilament drawing using S-1014 and later GE-177 glass was developed to prepare approximately 1-mil diameter filament at speeds from 50 to 1400 ft. per minute. The change in glass was made to obtain more refractoriness to permit the application of a pyrolytic carbon coating in the next task.

(2) Conductive Coatings - Various coatings and methods of applying them were considered as a means of providing a conductive coating for resistance or RF heating. These included: (a) Tungsten and Boron applied by indirect infra-red heating, (b) colloidal graphite suspensions applied by

dipping or wiping, and (c) vapor deposited carbon. The last approach was demonstrated in laboratory trials, but was not completely developed by the end of this program to the point of integrating it with the glass drawing operation. Colloidal suspensions were developed further in that they could be easily applied but gave a rougher surface, which may be detrimental to the strength and surface properties of the boron filament.

(3) Filament Heating Methods - Numerous dry contact brushes and wheel-type arrangements were considered as a means of eliminating the mercury contacts that are commonly used in present low-speed reactors. These various dry contacts were not nearly as attractive as RF heating which was then developed to the point where it will not only eliminate all direct contacts with the filament during processing but appears to offer the following other advantages: (a) higher average strength filament with lower variance, (b) lower conversion of diborane to undesired high polymers, and (c) the possibility for producing multiple filaments in a single reactor.

(4) Process and product improvement studies were primarily aimed at improving the deposition rate, tensile strength, and conversion of diborane to boron filament. A principal problem on which most of the attention was focused was the minimization or elimination of surface nodules which, due to the residual stress pattern in this type of boron filament, tend to be the cause of low tensile strength breaks. There appear to be numerous potential sources and causes for these occasional nodules which can be grouped under either (a) substrate coating defects or (b) high borane polymer particles formed and picked up on the filament during processing. The most likely location for the latter is on or around the mercury cups in the reactors used for most of these process studies. A great deal of detailed information on the hydride process was gained that provides a firmer basis for producing boron filaments in a high-speed reactor.

(5) Automatic Controls were considered to the point where selections can generally be made for usage in the next phase of the program.

Additional related topics including preliminary high-speed reactor design, plant layout, and filament costs are also discussed.

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## SECTION I

### INTRODUCTION

Advanced filaments and composites of a variety of compositions are being rapidly developed and promise very significant improvements in the materials performance for various portions of military vehicles. This work has been primarily done with boron filaments made from boron trichloride on a 0.5 mil tungsten substrate in a very expeditious and outstanding manner. The longer range view, however, suggests that a boron filament with an alternate substrate could provide several benefits which would permit greater applicability of composites, through lower filament costs, to military vehicles and weapon systems. Previous work at this laboratory as well as elsewhere indicated that potentially low-cost fused silica or various high temperature glasses could be used as the substrate, especially with a boron hydride as the source of boron. Among the benefits that have been demonstrated or in some cases indicated by preliminary work as advantages for the hydride boron-on-glass filaments are the following:

1. Lower overall density ( $\sim 2.30$  vs.  $2.70$  g/cc) which results in:
  - (a) comparable specific strength and modulus to boron-on-tungsten even though the absolute values are still somewhat lower.
  - (b)  $80,000$  ft/lb. vs.  $70,000$  ft/lb. for tungsten core material for 4 mil filaments.
  - (c) the potential for making 2 or 3 mil filaments which can permit filament reinforced composite panels with thinner gage thicknesses and smaller radii of curvature at little or no sacrifice in filament density or mechanical properties.
2. A higher coordination number for hydride boron (6 vs 5) and indications of greater thermal stability which may be advantageous in metal matrix applications.
3. In some cases a higher shear strength or more easily achieved wet strength retention in resin composites. This may be due to

the hydridic surface of the filament or to failure of conventional tensile tests of filaments to indicate their effective strength in the composite.

4. Predicted costs only 1/4 to 1/2 as much for boron on glass filaments as for boron on tungsten filaments in large quantities in the future. Current costs however are still rather high due to the limited production and therefore high cost of diborane.

This program has been particularly directed toward demonstrating the manufacturing feasibility of the individual technologies as they apply to subsequent integration into a high speed, in-line boron filament production process.

Each of the steps involved in achieving this challenging goal has been shown to be feasible and capable of such integration while permitting simultaneous refinements to be made in the process chemistry. Work performed under each of the four principal tasks in this program is described in the following sections.

## SECTION II

### TASK I - IN-LINE DRAWING OF GLASS SUBSTRATE

Objective: To develop equipment and procedures for drawing continuous monofilaments of refractory glass, at various speeds to 1000 ft. per minute for use as substrate material for the deposition of a conductive coating and boron.

#### A. BACKGROUND

Glass, because of low cost, useful properties, and the potential for constructing an in-line process, appears to offer the most potential for achieving a low cost substrate for the manufacture of CVD boron filaments. Most glass filaments are prepared in multiple filament form at very high speeds (10,000-30,000 ft./min.) and indeed achieve some of their high strength from this rapid drawing and consequent quenching in air. It was therefore necessary to develop a manufacturing process for glass monofilaments drawn at relatively low speeds (50-1000 ft/min.) which would be compatible with the rest of the integrated process for preparing CVD boron filaments.

Initially, S-glass which is quite widely used for high performance filament reinforced plastics was considered to be compatible with the overall in-line filament process. It was therefore used in the initial work on this program with very satisfactory results except that it only permitted the application of colloidal suspension-type carbon coatings under Task II. When these coatings were found to be insufficiently smooth and uniform, the need arose for a more refractory glass core which could be coated with pyrolytic carbon. A brief survey of several more refractory glasses (most of which were just becoming available during the summer of 1967) led to the choice of a new GE-177 glass. This change in glass necessitated changing from an indirectly heated platinum bushing to a directly resistance heated bushing. The drawing of both the S and 177 glass in the equipment developed and described here was very successful and is considered to be readily adaptable to the rest of the in-line CVD boron filament process work.

## B. HIGH-TEMPERATURE PLATINUM RESISTANCE FURNACE

### 1. General Approach

Of the two general approaches to melting and drawing glass from a bushing, it was decided to investigate first the feasibility of preparing the substrate filament in a tall, heavy platinum crucible placed inside an alumina muffle heated by a series of platinum wire resistance windings rather than the direct resistance heated bushing. Such an arrangement appeared to permit more precise control of the temperature in various parts of the furnace. Melting, refining, and filament-drawing (orifice) temperatures could be controlled separately. The glass could be melted in the upper part of the crucible at the highest temperature, refined at a slightly lower temperature, and drawn from the orifice at a still lower temperature. The fact that it was desired to be able to draw glass filament essentially 1 mil in diameter at rates as low as 50 feet per minute and as high as 1000 or more feet per minute made this arrangement more attractive. This scheme was thought to have the advantage of providing control of the viscosity of the glass over the widest range of values. Similar equipment had been used satisfactorily for the preparation of filaments of E-glass and related glasses<sup>(1)</sup>.

The temperature capabilities of this approach were recognized as being somewhat lower than those of an alternative approach, the use of a resistively-heated bushing. It was believed this situation was compensated for by the selection of Ferro S-1014 glass as the material to be melted and drawn first. This glass has essentially the same softening point as conventional S-glass, but appeared to be capable of being melted and fiberized at temperatures about 100°C lower than the corresponding requirements for other S-glass.

Construction of a high-temperature platinum resistance furnace incorporating these ideas was completed, and a platinum crucible with a spinnerette-type orifice was put in place during the first quarter of the program. The furnace, described in more detail below, comprised four resistance



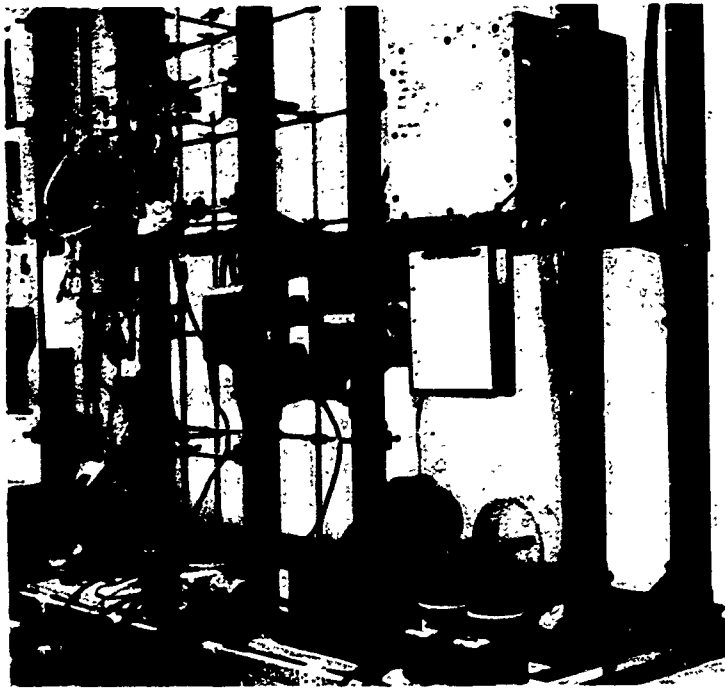
units, each regulated by its own variable transformer and each monitored by a separate thermocouple. A control circuit was devised and installed for holding the furnace at fixed temperatures. Relays controlled the supply of electric power to the two major resistances in accordance with the signal received from one of the thermocouples. As originally arranged, the two guard heaters remained "on" all the time the furnace was being operated. The temperature of the furnace was checked periodically with an optical pyrometer.

The furnace and its controls are pictured in Figure 1. The four-point thermocouple switch, the temperature indicator-controller and the relays are situated just below and to the left of the furnace. The performance of the empty furnace was determined first, during a period of several days. The electrical characteristics of each of the resistance windings were determined separately, with a view to providing optimum control of the units. Typical voltage, amperage, and transformer settings were recorded for holding the furnace at various temperatures. This was followed by numerous runs to make glass monofilament as described later.

## 2. Construction Features

### (a) Furnace

The chief features of the high-temperature furnace are shown in Figure 2. The core of the furnace consisted of three alumina muffle tubes, separated by or supported by alumina rings. Platinum-rhodium resistance coils were wound around the alumina tubing. Resistances No. 2 and No. 3, the melter and refiner heaters respectively, were made of 40-mil platinum-40% rhodium wire. Resistances Nos. 1 and 4, guard heaters, were of 20-mil platinum-40% rhodium wire. (No. 4 was used also to help control the temperature of the orifice.) The two upper pieces of alumina tubing had an internal diameter of 2 inches while the lower section had 2 3/16 inches i.d. All sections had about 3/16 inch wall thickness. The resistance wire was held in place by refractory alumina cement. The locations of the thermocouples and the electrical leads for the resistances are shown in



**Figure 1. High-Temperature Platinum Resistance Furnace and its Controls for Melting Glass and Drawing Substrate Filament.**

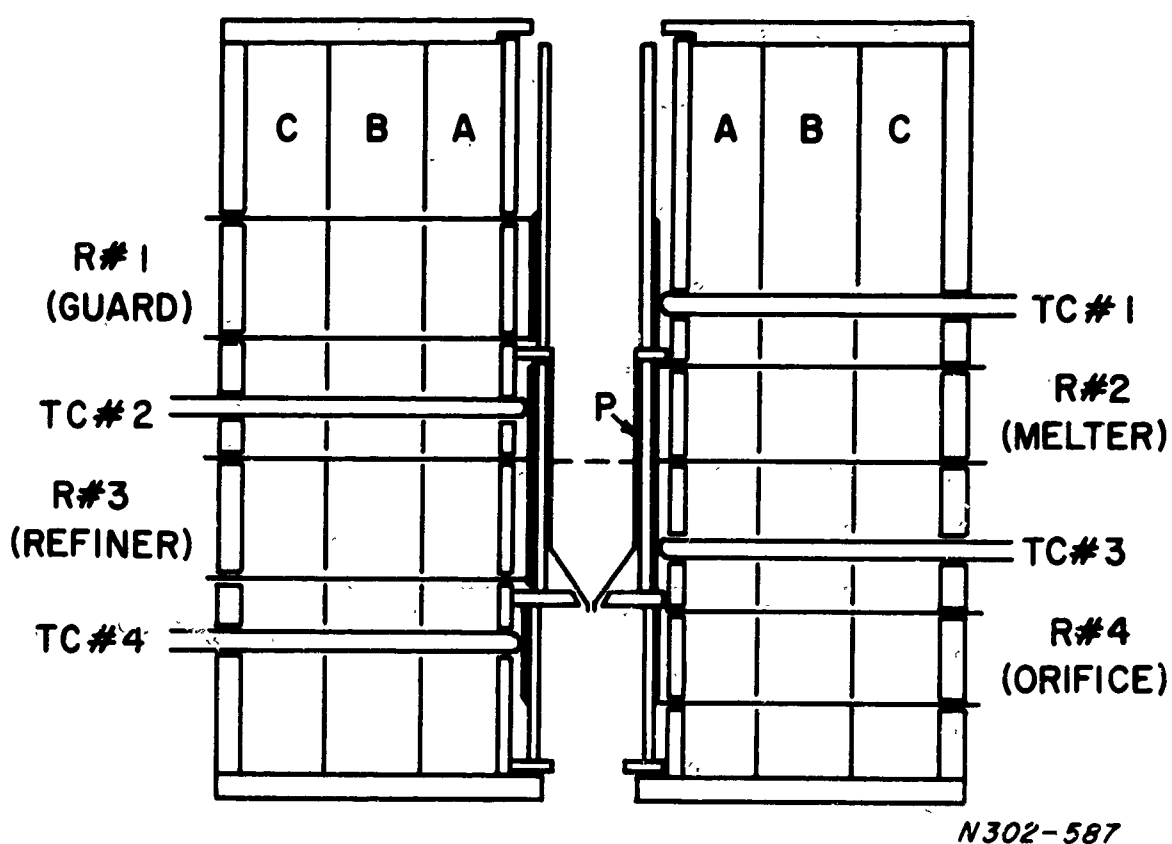


Figure 2. General Construction of the High-Temperature Furnace, R = Resistance Winding, TC = Thermocouple, P = Platinum Crucible, A = Powdered Alumina, B = Insulating Firebrick, C = Block Insulation.

this figure. Thermal insulation was provided by the following sequence of materials: (a) powdered high-purity alumina, (b) refractory insulating firebrick, (c) Superex-type block insulation and (d) 1/2 inch Transite for the shell of the furnace.

The position of the platinum crucible is indicated in Figure 2. The crucible itself is illustrated in further detail in Figure 3. The crucible was 1.75 inches in diameter and had an over-all height of 5 inches. It was made of 40-mil thick platinum-20% rhodium. A screen, with openings 1/4" in diameter, held the glass marbles while they were being melted. It was considered important to keep cold marbles from dropping to the bottom of the crucible of molten glass as they otherwise would do in the absence of the melting screen. It was estimated that one 3/4-inch flass marble contained enough glass for about 23,000 feet of 1-mil filament. Accordingly, once a sufficient amount of glass had been melted, it would have been necessary to add one marble every 460 minutes if drawing continuously at 50 feet per minute or once every 23 minutes if pulling 1000 feet per minute, to maintain the level of molten glass in the crucible.

#### (b) Technical Considerations

A number of technical considerations were of influence in the selection of materials and in the construction and operation of the furnace. Among these, the following are noteworthy:

The alumina muffles were made of dense, impervious, recrystallized high purity alumina tubing. The top use temperature of this material is cited as 1950°C.

The crucible was made of platinum-20% rhodium, a composition that represents a balance of refractoriness, high-temperature strength and ease of fabrication.

For the high-temperature thermocouples, the system platinum-6% rhodium vs. platinum-30% rhodium was selected. Such thermocouples have been calibrated to 1820°C, which is significantly above the top use temperature recommended for platinum vs. platinum-10% rhodium or

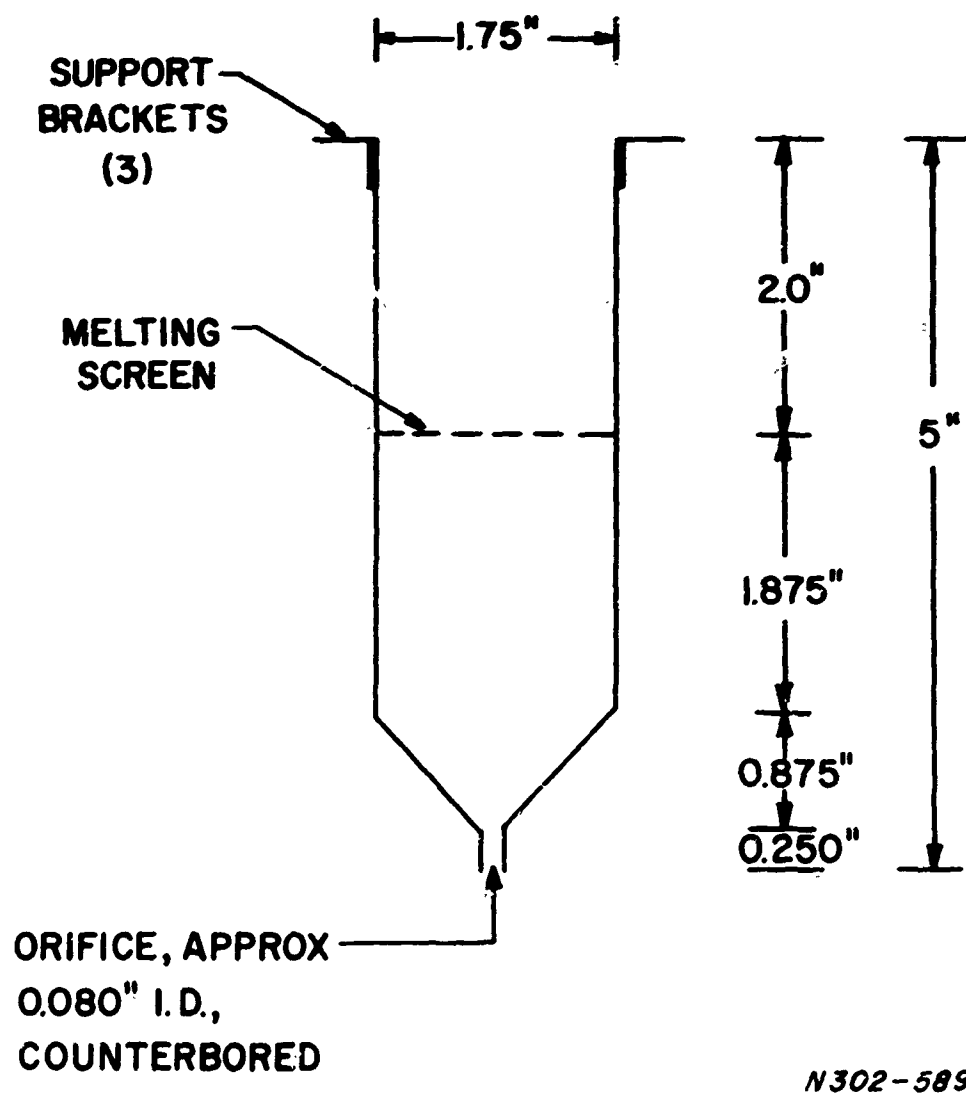


Figure 3. Crucible of Platinum -20% Rhodium, 0.040 Inch Thick, with Spinnerette-Type Orifice.

platinum vs. platinum-13% rhodium, which is a common combination for high temperature use.

Platinum-40% rhodium was chosen for the resistance wires. The refractoriness of the metal increases with the rhodium content of the alloy, but the stiffness and the brittleness also increase. The melting point of this alloy is reported to be about 1950°C but its top use temperature, of course, is lower. The resistance of platinum-40% rhodium increases less with increase in temperature than does that of platinum itself. For example, the resistance of platinum-40% rhodium at 1400°C is about 2.9 times the room temperature value, while that of platinum wire at 1400°C is more than five times the room-temperature resistance.

The maximum current density (amperes per square inch) is very much a function of temperature. The relationship is shown in the following table, along with corresponding values calculated for 40-mil and 20-mil wire.

TABLE I  
CURRENT DENSITY VS. TEMPERATURE, PLATINUM-  
RHODIUM RESISTANCE WIRES

Temp. °C	Current Density Amps./Sq. In.	Corresponding Limits, Amps.	
		40-Mil Wire	20-Mil Wire
1000	36,000	45.2	11.3
1200	26,000	32.7	8.1
1400	18,000	22.6	5.6
1600	12,000	13.5	3.8
1800	8,000	10.0	2.5

There also appears to be a general relationship between the major variables encountered in drawing glass filament. For example, Phillips<sup>(2)</sup>, analyzing a report by Thomas<sup>(3)</sup>, developed a statement

$$D^2 = \frac{69Hd^2}{N\eta}$$

Where D = Diameter of the filament in inches

N = Rate of pull, feet per minute

$\eta$  = Viscosity of the glass, poises

H = Head of glass, in inches

d = Diameter of orifice, inches

Although this relationship was deduced from data covering a range of head from 1 to 2.25 inches, of N from 500 to 8000 feet per minute and of  $\eta$  from 9.2 to  $3.16 \times 10^3$  poises, it has promise of being valid over a wider range of conditions. Although it was not necessary to use this in a precise manner, the above generalization served as a very useful guide in the selection of operating conditions for drawing glass filament in this program.

### C. FILAMENT DRAWING OF S-GLASS AND LOWER MELTING GLASSES

Three glass compositions were successfully filamented at various speeds during the second quarter. The glasses, a soda-lime glass, Pyrex glass, and S-1014 glass, required successively higher temperatures for the drawing of filaments.

Early in the quarter, the high-temperature platinum resistance furnace was remodeled with the original top and bottom heating units, but having a new resistor winding for the melter zone. Resistance windings Nos. 2 and 3, as shown in Figure 2, were replaced by a single resistance unit. Optical pyrometer readings were made to determine the temperature of various points in the platinum melting crucible and the refractory core of the furnace. These temperatures were compared with the temperatures indicated by the nearest thermocouples, which might be several inches away. Because of their locations, the thermocouples invariably showed lower temperatures than those determined directly by the optical pyrometer. The thermocouples were valuable in monitoring various parts of the furnace continuously, showing whether any zone was becoming hotter or colder, for example. However, significant temperatures within the crucible and at the orifice were measured with the optical pyrometer.

#### 1. Soft Glass

It was decided to check the performance of the orifice first with a soda-lime glass having a moderate melting temperature. Twenty-one clear glass marbles of the type used in chemical condensation columns, each 1/2 inch in diameter, were placed in the melting crucible at about  $1340^\circ\text{C}$ . The temperature of the orifice zone was kept relatively low, around  $900^\circ\text{C}$ ,

by reducing the amount of power in the lower guard heater (heater No. 4, Figure 2) and also by blowing a small stream of nitrogen toward the orifice. The glass was thus melted and refined overnight.

The next morning, the nitrogen stream was discontinued and the temperature of resistor No. 4 was raised slowly. A temperature soon was reached (about  $1150^{\circ}\text{C}$ ) at which the glass in the orifice became soft enough to flow. At the appropriate viscosity, glass filament was readily drawn from the orifice.

Roughly 3000 feet of filament were wound onto spools at 50 feet per minute, in three separate runs. A 600-foot length was drawn first, but this test was discontinued when it was decided to use a different type of spool. Some 1500 feet was put on a second spool, and roughly 800 feet on a third. The temperature of the orifice was then increased slightly, while the melting zone was unchanged, and about 900 feet of filament was spooled at 100 feet per minute. The temperature was raised still further, and between 900 and 1500 feet of filament was pulled at 150 feet per minute. Micrometer measurements of the filaments showed that the diameters ranged between 1 and 2 mils, but most of the material was between 1 and 1.2 mils in diameter. It was felt that these trial runs demonstrated that the orifice was properly designed for these low rates of draw.

The temperatures of the melting zone and the orifice were then increased further, and the balance of the glass in the platinum crucible was drained into a container of water.

## 2. Pyrex Glass

It was decided to melt and pull filaments of a glass having a higher melting point, to check the operating characteristics of the furnace and orifice at a level about  $200^{\circ}\text{C}$  higher than the initial runs, and to provide additional continuous lengths of filament for use in carrying out the activities of Task II. Accordingly, the crucible was then charged with Pyrex glass. For this purpose, short lengths of chemical glassware tubing served as the feed material.



Pyrex glass fiberized readily when the temperature of the bottom of the crucible was around  $1250^{\circ}\text{C}$ . The molten glass itself was held at a higher temperature, generally  $40^{\circ}$  to  $90^{\circ}$  above that of the bottom of the crucible. Approximately 5000 feet of Pyrex filament was drawn at 75, 125, and 175-200 feet per minute. The filament appeared to be of good quality and uniform diameter, although it seemed to be somewhat brittle. It should be noted that Pyrex glass was not developed for the purpose of making filament. In view of these results, it seemed appropriate to consider immediately the pulling of filament of a still more refractory glass. At the conclusion of these runs, the balance of the Pyrex glass was drawn from the crucible and was replaced with S-1014 glass.

### 3. S-1014 Glass

The S-1014 glass, fed into the crucible as  $3/4$  inch marbles weighing about 10 grams each, proved easy to draw once the proper temperature conditions had been established. The early filament pulled from the orifice was lumpy. The appearance led to the belief that a small amount of the previous glass might have remained in the crucible and failed to mix thoroughly with the S-1014 glass. In effect, the lumpy glass was flushed from the crucible by placing additional marbles of S-1014 glass on the melting screen; subsequent filament was free of inclusions. Droplets of glass allowed to drain from the orifice and fall into a container of water were quite clear and seemed to be almost of optical quality.

The temperature of the platinum crucible generally was maintained at  $1400^{\circ}\text{C}$  or higher for melting the marbles. The bottom of the crucible was between  $1320^{\circ}\text{C}$  and  $1355^{\circ}$  during the pulling of filament. Glass was drawn at rates of 75, 125, 175 and 400 feet per minute. A continuous filament of 2960 feet was drawn at 75 feet per minute. Later, some 26,000 feet of continuous length was spooled by drawing at 400 feet per minute for 65 minutes. The drawing operation presumably could have been continued indefinitely, but it was stopped at this point because of mechanical difficulties with the winding equipment. There was no evidence to indicate that the

top rate of draw for this orifice was being approached, but 400 feet per minute was the maximum speed of the winding apparatus then in place.

At the conclusion of this series of runs, the S-1014 glass was removed from the crucible and the furnace was cooled and inspected. The crucible and the furnace windings were found to be in good condition. In the interest of closer temperature control, the single melter-refiner resistance winding used in the previous campaign was replaced by two separate resistance units, one for the melting region and one for the refining zone, as had been used originally and as is shown in Figure 1. The furnace was reassembled and returned to operating temperature, and the platinum crucible was charged with fresh marbles of S-1014 glass.

Studies were then undertaken of various procedures for coating freshly-drawn glass filament with a conductive film, on a routine basis. Compositions investigated and deposition techniques studied are discussed under Task II. A variety of arrangements of pulleys, coating drums, and furnaces were investigated. No difficulties were encountered in drawing S-1014 glass filament, changing direction around an eight-inch diameter pulley, and level-winding onto an eight-inch drum. Filament breakage was practically eliminated when the pieces of equipment were brought closer together.

The winder previously used had been satisfactory for the original purpose, but it developed a considerable amount of vibration at the higher speeds and was limited to a top spooling rate of 400 feet per minute. Consequently, a new, more versatile level winder was built and put in operation. With the new winder, filament of S-1014 was pulled and spooled directly over a wide range of speeds: as slow as 40 feet and as fast as 1400 feet per minute.

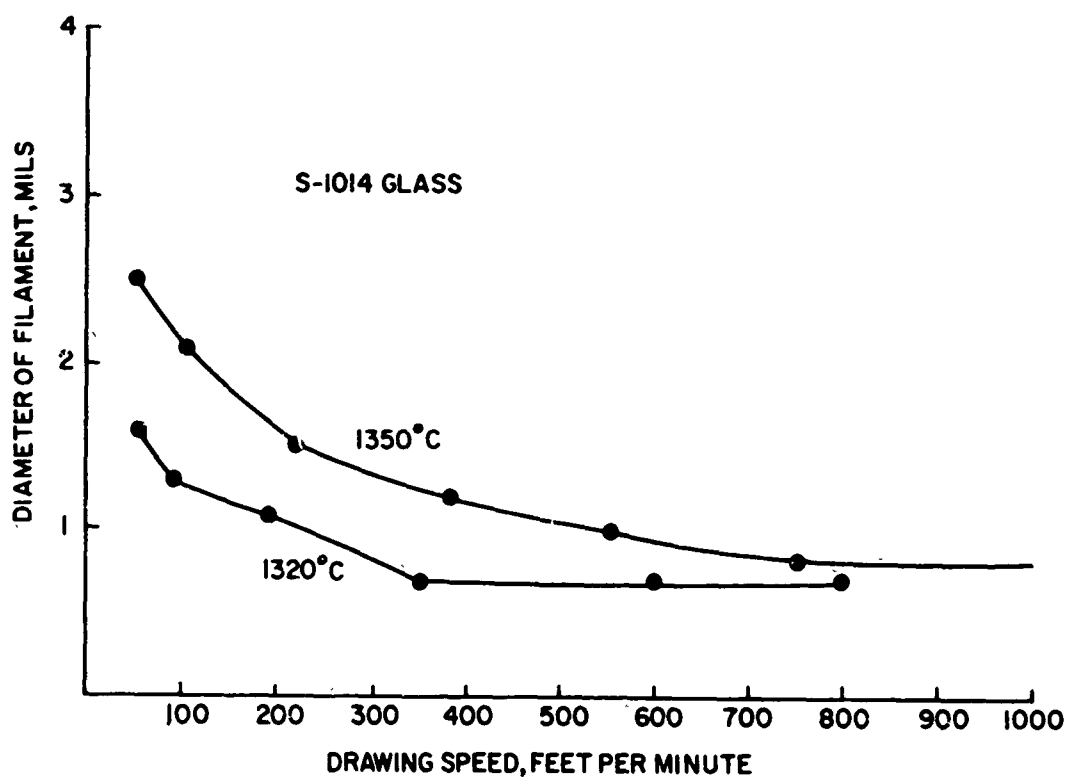
A systematic study was then made of the influence of temperature and speed of draw on the diameter of filament formed. Roughly 500 to 1500 feet of filament was pulled under each of a series of temperature and speed conditions. Five to ten measurements of diameter were taken in each of

six different regions along each length of filament. The results of these measurements are shown in Table II and Figure 4. The higher the temperature and the slower the speed, the larger was the diameter of filament drawn from this orifice. The effects of variations in temperature or speed were seen to be reduced at the higher speeds of operation. Thus it was found that by varying the temperature, the S-1014 glass could be drawn at essentially any speed and diameter required for the integrated process.

Later in the third quarter, a plug of devitrified material tended to close the orifice from which the glass filament was being drawn. It was decided to cool the furnace, remove the platinum crucible, and clear the orifice. This was accomplished successfully and the crucible again was found to be in good condition. New alumina disks were cast and fired, for use in reassembling the furnace.

TABLE II  
RELATIONSHIPS BETWEEN DRAWING SPEED, TEMPERATURE  
AND FILAMENT DIAMETER OF S-1014 GLASS

1320°C		1350-1355°C	
Rate of Draw Ft./Min.	Filament, Diameter Mils..	Rate of Draw, Ft./Min.	Filament Diameter, Mils.
56	1.6	56	2.5
96	1.3	104	2.1
192	1.1	224	1.5
360	0.7	384	1.2
600	0.7	554	1.0
800	0.7	760	0.8
		1400	0.6



N 302-689

Figure 4. Diameter of S-1014 Filament as Influenced by Temperature and Speed of Drawing.

#### D. INVESTIGATION OF OTHER REFRACTORY GLASSES

It was recognized that it would be desirable to utilize glass having a softening point even higher than that of S-glass in order to permit the use of higher temperatures of operation in either the preparation of the conductive coating or the boron deposition reactor, or both. Accordingly, three more-refractory glasses were selected for investigation and samples of these were obtained. The glasses were General Electric Company (Lamp Glass Department) glasses No. 175 and 177 and Corning Works Glass No. 1716. Their properties are listed in Table III along with the properties of S-1014, Vycor, and fused silica for comparison.

Filaments of both 1716 and 177 were pulled readily from the rod or cane, in preliminary examination of these glasses. These glasses offered softening points roughly 160 and 200 degrees greater than S-glass. Attempts were not made to melt these glasses in the equipment used for S-1014 glass. It was felt that the furnace and crucible might have to be operated too close

TABLE III

## PROPERTIES OF POTENTIAL SUBSTRATE FILAMENT GLASSES

Glass Designation	Mfr.	Liquidus Temp. °C	Approx. Bushing Control Temp. °C	Softening Point °C	Anneal Point °C	Strain Point °C	Coefficient of Expansion per °C 0-300°C
S-1014	Ferro	1220	1350	930-940	-	700	$42 \times 10^{-7}$
175	G.E.	1445	1520	1060	-	834	$35 \times 10^{-7}$
1716	Corning	1350	-	1106	861	805	$35.2 \times 10^{-7}$
177	G.E.	1260	-	1145	862	814	$40 \times 10^{-7}$
2-55-3	G.E.	1380	-	1165	895	830	$40.2 \times 10^{-7}$
Vycor	Corning	-	-	1500	910	820-890	$8 \times 10^{-7}$
Fused Silica	G.E. Corning, etc.	1700	2200 <sup>+</sup>	1670	1050	990	$5.6 \times 10^{-7}$

to, or above, the design limits if they were employed to melt these more refractory glasses. On the basis of these studies, work was undertaken to design, assemble, and put into operation a resistively-heated platinum bushing capable of being used to melt and filamentize glasses more refractory than S-1014. The GE-177 material appeared to be the most promising of these higher-melting glasses from the standpoint of availability, temperature characteristics (liquidus temperature, softening, anneal and strain points), and good thermal expansion match with boron.

#### E. RESISTANCE HEATED BUSHING

With the need for a more refractory glass due to coating requirements to be used as the core of boron filament, a new direct heated bushing with an SCR control circuit was constructed. It is described below.

The SCR control and furnace circuit (shown in Figure 5) accepts the input from a thermocouple and, after appropriately processing the dc voltage from the thermocouple, drives a pair of silicon controlled rectifiers which in turn control the current to the primary of the furnace transformer. The operation of the device can be described by reference to the circuit diagram shown in Figure 5.

The input signal from the thermocouple is fed into a double ended differential pre-amplifier whose function is to amplify the dc signal of a few millivolts to a level of about 0.5 volt. The signal is then fed into an operational amplifier, which has a gain of 10. The operational amplifier block serves two functions other than providing gain. First, the operational amplifier characteristics are used to provide the feedback compensation which prevents the system from oscillating. Second, the operational amplifier also acts as a summing device which algebraically sums the signal with a variable reference voltage. The algebraic sum of these two voltages provides the dc error signal which ultimately controls the current to the furnace. The dc error signal is fed into a circuit which provides pulses to drive the SCR block which vary in phase with the 60-cycle line frequency. These pulses turn on the silicon controlled rectifiers at the

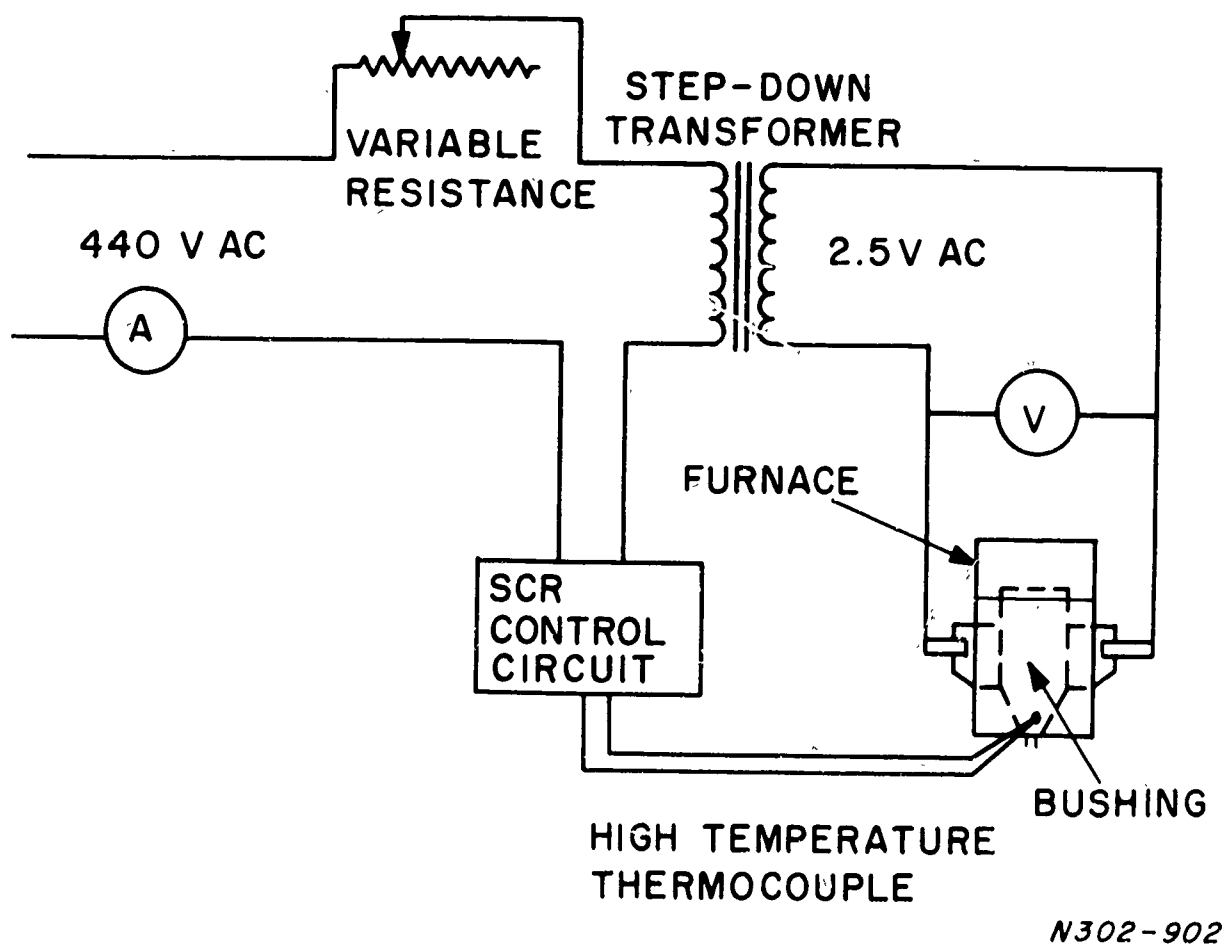


Figure 5. Electrical Circuit for Direct Resistance Heated Glass Drawing Bushing.

proper time in each half cycle to provide the correct current into the furnace transformer primary.

In operation, the SCR control circuit is simply connected to the source and the transformer, the thermocouple leads are connected, and the power is turned on. The appropriate temperature is set on the front panel and the controller will then maintain this temperature within the limits required. It is necessary to provide a surge protection resistor during warmup of the furnace in order to protect the system from excessive currents while the bushing resistance is low. The general dimensions of the high-temperature bushing, which was made of platinum-20% rhodium, are shown in Figure 6. The bushing was encased in high-temperature insulating brick (Babcock and Wilcox K-3000), held in place by a steel shell. Sheets of 200-mil Kaowool paper, (Babcock and Wilcox) were placed between the brick and the metal for additional thermal insulation. The completed furnace is pictured in Figure 7. As is the practice in this type of filament-drawing facility, the bushing serves both as the electrical resistor and as the container for the molten glass. Power was supplied by a 5 KVA step-down transformer which reduced 440 volt ac to 2.5 volts. The primary of the transformer was controlled by an SCR in response to the e.m.f. from a high-temperature thermocouple (platinum-6% rhodium vs. platinum-30% rhodium) spot-welded to the bushing near the orifice. The current required for operating the bushing at glass filament-drawing temperatures was of the order of 1000 amperes at 1.5 volts.

The bus-bar leads from the secondary of the transformer, as well as the terminal blocks for the attachment of the bushing, were water-cooled. Electrical interlocks were inserted in the control circuitry to interrupt the current (1) in the event of low water pressure; (2) if the bushing should reach an undesirably high temperature, or (3) if the temperature-sensing thermocouple should break.

On the first runs of the furnace to low temperatures (between 500 and 600°C), a small but troublesome amount of arcing was noted between the



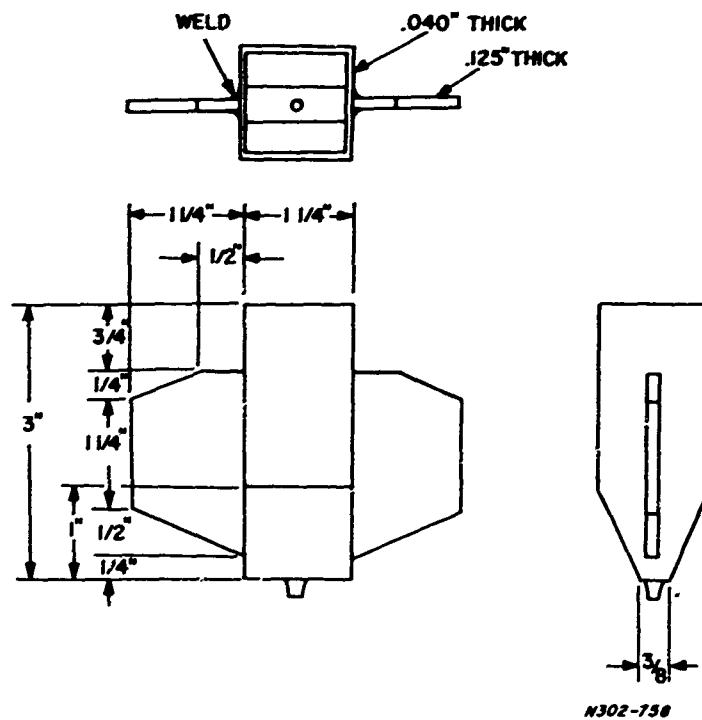


Figure 6. Resistively-Heated Bushing for Melting and Drawing Filaments of High Temperature Glass.

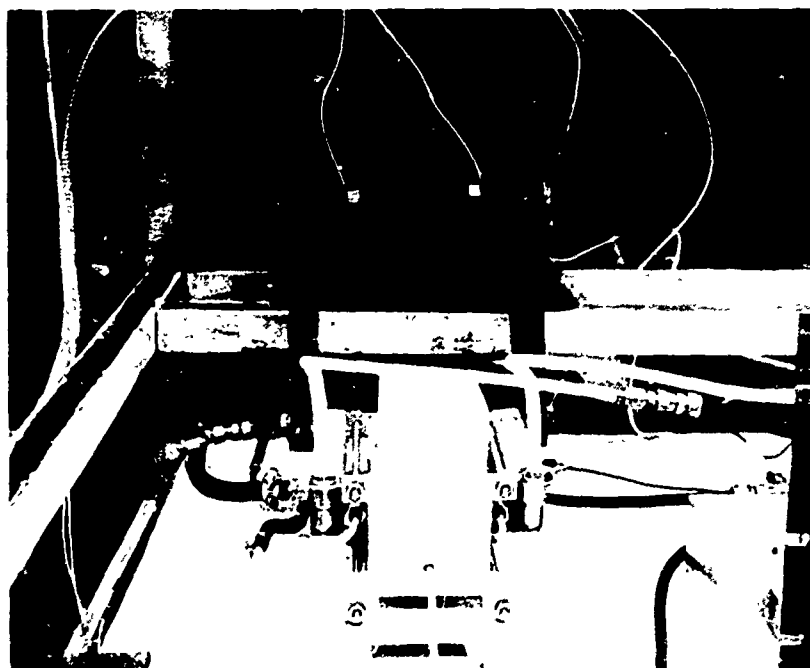


Figure 7. Photograph of Resistance Heated Bushing Furnace.

copper grips of the bus bars of the step-down transformer and the contact lugs of the platinum bushing. This arcing served to roughen both the copper and the platinum in limited areas. Small amounts of copper seemed to be transferred to the platinum surface. The lugs appeared to become heated, in the neighborhood of the arcing, faster than the body of the bushing. Finally, it was observed that the arcing tended to produce a signal that interfered with the operation of the electronic circuit for the SCR power control.

New grips were designed, machined and installed. They provided a faster, more convenient, and more flexible means of making contact. As an additional feature, platinum foil shims were placed between the copper terminal pieces of the bus bars and the platinum lugs of the bushing. So far as could be determined, the new arrangement was quite superior to that originally provided and effectively controlled the arcing.

Near room temperature, the platinum bushing acts essentially as a short across the secondary of the transformer. It was found necessary to insert a resistance in the 440 volt primary circuit to help limit the surge of current when the bushing is first activated. In the early runs, moderate-duty fixed resistors proved inadequate for this purpose. Heavy duty rheostats were then selected because of their current-controlling capacity and because the amount of resistance can be reduced as desired when the bushing is approaching top operating temperature. Specifically, five 100-ohm, 1 KW variable rheostats in parallel provided up to 20 ohms resistance at 5 KW when needed. Current surges were seen less frequently when the furnace had been held at a given temperature long enough to reach an equilibrium condition.

A series of experimental runs, ranging in length from several hours to approximately 55 hours, was carried out for the purpose of checking the operation of the various components of the system and for determining the control characteristics. There was nearly a linear relationship between the control point settings of the SCR circuit and the resulting furnace temperature. The bushing responded to changed control settings and assumed a new temperature rapidly and reproducibly.

Drawing of about 1 mil diameter 177 glass filament was then routine for use in Task II developments. The molten glass was held overnight at about  $1200^{\circ}\text{C}$ . When it was desired to draw filament, the bushing temperature was raised to around  $1480^{\circ}\text{C}$ - $1500^{\circ}\text{C}$ . The highest bushing temperatures normally recorded while drawing glass was  $1530^{\circ}\text{C}$ , but temperatures as high as  $1585$ - $1600^{\circ}\text{C}$  were reached for exploratory purposes. Glass was drawn successfully at rates from 15 feet per minute to nearly 400 feet per minute. No attempt was made to pull filament at higher speed. However, inasmuch as the orifice of the bushing had the same dimensions as the platinum crucible used earlier (with S-1014 glass), there is no reason to assume that drawing would not have been equally successful at 1400 feet per minute, for example, if this had been required.

The temperature-viscosity relations of this glass seemed quite appropriate for the drawing of filaments. There was no tendency for the glass to drip from the orifice at the "hold" temperature of  $1150$  to  $1250^{\circ}\text{C}$ . When the bushing temperature was raised to about  $1500^{\circ}\text{C}$ , a small amount of glass appeared at the bottom of the orifice, from which a filament could be started readily. At still higher temperatures a larger amount of glass tended to extrude itself, with time, somewhat as an elongated bead or thin rod.

### SECTION III

#### TASK II - CONDUCTIVE COATINGS

Objective: To place a compatible and continuous electrical coating on a glass monofilament as it is drawn from the melt.

##### A. BACKGROUND

As has been stated earlier, the use of a continuous glass monofilament as a substrate for subsequent deposition of boron from diborane in a continuous integrated manufacturing process offers several economic advantages. In addition to the lower raw material cost per pound of filament for substrate compared to tungsten or silica, less handling (spooling and subsequent mounting and dereeling and storage) would be required, with consequent lower labor costs. However, only the substrate itself can be heated during deposition of boron because diborane reacts readily at any warm or hot surface. In order to accomplish this, an electrically conductive coating must be placed on the substrate, permitting the deposition to be carried out in a hot-wire, cold wall reactor.

In considering which approaches appear to be most promising for carrying out this step of the integrated manufacturing process, the requirements of both coating and deposition steps plus chemical and physical compatibility with the boron must be considered. In the light of the restrictions placed on these processes by the physical characteristics of the glass itself, and by the properties and characteristics of the coating material, the glasses used in this program, designated S-1014 and GE-177, were chosen on the basis of their thermal expansion compatibility with the boron coating, and their ability to withstand the processing conditions prevailing during boron deposition, as well as the basic requirements of availability, cost, and ability to be drawn from the melt at reasonable speeds. The properties of these glasses were listed in Table III. Their relatively lower melting points, compared to silica and tungsten, and consequent low strength at elevated temperatures restricted the choice of coating processes to low and intermediate

temperature thermal decomposition processes and suspension coating. Other processes such as dipping, evaporation, sputtering, etc. were ruled out because of high cost, low rate, or incompatibility of the coating with boron.

The low temperature decomposition or pyrolysis processes (up to about  $500^{\circ}$ - $600^{\circ}$ C) were based on the use of tungsten hexacarbonyl, tungsten hexafluoride in hydrogen, and diborane, each of which yields a solid coating at suitable surface temperatures. The suspension coating approach made use of commercially available, finely divided (ca. 0.5 micron) graphite suspensions in aqueous media, while the moderate temperature pyrolysis process consisted of carrying out the thermal decomposition of preheated small hydrocarbon molecules (acetylene, methane, propane), when passed over the hot filament surface. The last mentioned approach is the most desirable since it involves the use of inexpensive raw materials and leaves a thin, smooth coating of low atomic weight. The first approach was the least attractive from the standpoint of cost and density, while the suspension method appeared to be the simplest to carry out in a practical sense. The experimental program and results are described next.

#### B. LOW TEMPERATURE PYROLYSIS (CVD) PROCESSES

Chemical vapor deposition processes consist of those in which reaction or dissociation of gaseous components, either in the gas phase or at the deposition surface, produces species which comprise the material to be deposited. In order to be efficient with respect to deposition on the filament surface alone, which has an extremely small area compared to that of the reaction chamber, it was necessary to introduce heat to the filament by a means other than radiation or conduction from an externally heated wall. In other words, the formation of the conducting film should be carried out in a hot-wire cold wall reactor in order to be efficient as well as controlled. Because the substrate was initially non-conducting, heat had to be introduced indirectly, for example, by inertial preheating, with an electrically heated oven or by conserving the heat remaining in the filament immediately after drawing. Another approach was to use focused infrared radiation such as is provided by quartz lamp line-heaters equipped with a suitably designed

reflector. When the filament was sufficiently strong at elevated temperatures, e.g. quartz or Vycor, flame deposition could also be used. This was not feasible, however, for S-1014 or GE-177 glasses of interest in this program.

The deposition process itself is limited by the rate achievable at the maximum allowable temperature. In the cases under consideration, recalling temperature and compatibility limits, the deposition of tungsten from tungsten hexacarbonyl ( $W(CO)_6$ ) and tungsten hexafluoride ( $WF_6$ ) were investigated as applied to S-glass, while acetylene decomposition was studied with respect to its suitability for GE-177 glass. The direct deposition of boron from diborane was also tried on an S-glass substrate. All of these reactions, except acetylene decomposition, can be carried out at reasonable rates at temperatures less than  $600^\circ C$ .

#### 1. Tungsten Deposition on S-Glass

##### (a) Tungsten Carbonyl Decomposition

The formation of thin tungsten metal films had been studied in the previous program<sup>(4)</sup> by using resistively heated carbon coated fused silica (0.7 mil diameter) as a substrate in an atmosphere of flowing argon carrying a small percentage of tungsten hexacarbonyl. Resistances between 6000 and 100,000 ohms/in. were obtained depending on the power supplied to the filament. Filament temperatures could not be determined below the radiant limit because of the small radiant area involved. A similar approach was used with prespooled sized S-1014 glass monofilament, 1.0 mil in diameter (Ferro Corp., Cleveland). The experimental arrangement is shown schematically in Figure 8. The Pureco Oil filament sizing was removed by passing the filament through a methylene chloride bath and beneath a heat lamp prior to entering the carbonyl reactor. The latter was a quartz tube, 1/2" O.D., provided with suitable side arms and end plugs. Heat for the decomposition was supplied by a quartz lamp line heater focused on the filament through the reactor wall. Cooling air was blown between the quartz lamp and the reactor in an effort to prevent the wall from reaching a temperature at which decomposition could occur.

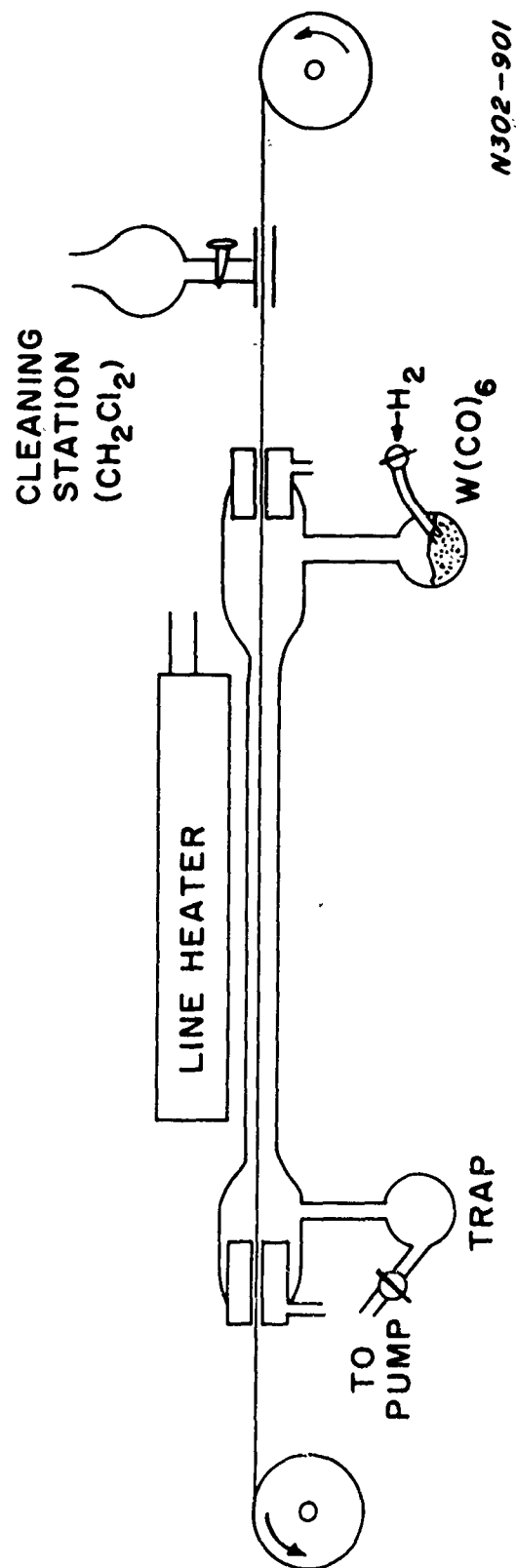


Figure 8. Apparatus for Coating from Tungsten Carbonyl Using Focused Radiation.

A series of experiments was carried out at both atmospheric and reduced pressure which demonstrated the principal problems associated with this approach to heating a filament indirectly. At atmospheric pressure, deposition occurred principally in the gas phase, producing a sooty deposit on the filament which, although conductive, was easily wiped off. When the walls were cooled sufficiently to prevent this, the filament temperature decreased to a level below that at which deposition could occur efficiently at its surface.

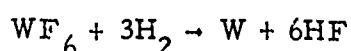
At reduced pressure, deposition on the wall occurred rapidly enough to cause the wall to become opaque to the radiation. This resulted in an increase in wall temperature and further deposition there, with no deposition on the filament itself.

As a result, this method of achieving a conductive coating was set aside until a freshly drawn filament, carrying some residual heat, could be used as the substrate, or a better system substituted. Eventually economic and end-use considerations mitigated against the use of tungsten films for this purpose and no additional work was done with this system.

Concurrent with these efforts, an approach to the same goal was tried which involved passing a prespooled and cleaned S-glass monofilament through a pyrolytic graphite preheater and into a carbonyl reduced pressure reactor as shown in Figure 9. The rate of heat loss from the filament proved to be too high for its surface temperature to be in the deposition range when it entered the reactor. Preheater temperatures were raised until the filament parted due to its low strength at these temperatures (600-700°C). This approach to achieving a conductive coating was also set aside at this point.

#### (b) Tungsten Hexafluoride Reduction

An approach similar to that just described but perhaps more readily controlled due to its higher thermal requirement is that of reducing tungsten hexafluoride with hydrogen:





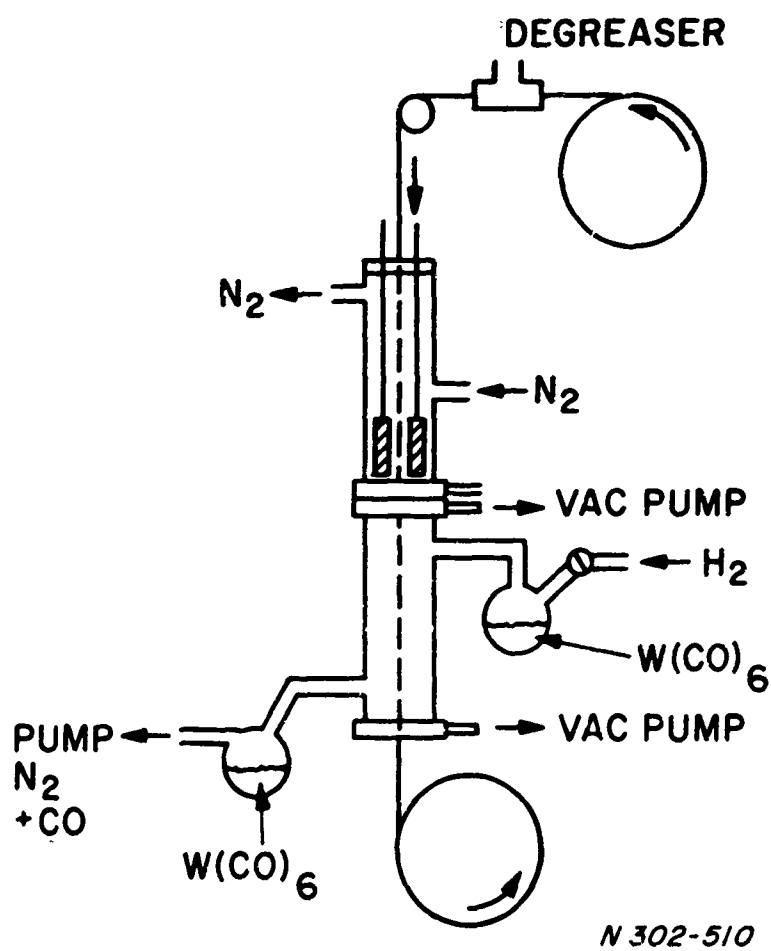


Figure 9. Filament Heating and Gas Handling System for Deposition of Tungsten from Tungsten Carbonyl.

This reaction was studied in apparatus similar to that shown in Figure 8. Here again however, reduction of tungsten at the reactor wall, with subsequent blocking off of radiation to the filament proved to be the chief obstacle to success, and the approach was not studied further.

## 2. Diborane Decomposition

Diborane commences to decompose to its elemental components at approximately  $700^{\circ}\text{K}$  ( $523^{\circ}\text{C}$ ) and is as much a candidate for low temperature deposition on a glass substrate heated indirectly, as it is to deposit boron to prepare 4.0 mil boron on an electrically heated glass filament. Earlier work<sup>(4)</sup> had indicated that boron could be deposited directly on S-glass by this approach, utilizing focussed infrared radiation to heat the filament. At that time, although boron was indeed deposited on S-glass, the formation of higher boranes (yellow solids) rendered the conditions applied then unsuitable for continuous operation. Further studies along these lines on this program confirmed this conclusion and no further work was carried out using diborane in conjunction with focussed radiation as a heat source for the filament.

## C. GRAPHITE OR SUSPENSION COATING

A common technique for placing a conductive coating on a non-conductive substrate is to use any of several commercially available graphite suspensions. These consist of graphite particles, 0.5 to 3 microns in diameter, depending on the need, suspended in an aqueous vehicle which usually contains a volatile suspension agent and a binder. The latter is generally a sodium silicate. Some baking is required to drive off moisture and to provide a hard adherent coating. Table IV lists the properties of those obtained for use on this task.

From the standpoint of existing technology and simplicity of equipment design (low temperature, open atmosphere, rollers, ovens, etc.) this appeared to be a promising technique to explore. Initial studies were performed using prespooled S-1014 monofilament, supplied on paper collets and coated with a hydrocarbon sizing. The principal areas for exploration were to determine which aspects of a coating process had the most effect on

TABLE IV  
CHARACTERISTICS OF VARIOUS GRAPHITE COATINGS

<u>Name</u>	<u>Part Size</u>	<u>Medium</u>	<u>Wt % Solids</u>	<u>Supplier</u>
1. Aquadag	$\sim 0.5\mu$	Water	22	Acheson Colloid Co.
2. Graphilm	$\sim 2.5\mu$	Water	35	Asbury Mills Inc.
3. RCA	$\sim 2.5$	Water	35	RCA Inc.
4. Dixon 94-22	$80\% < 1\mu$ $20\% > 1\mu$	Water	22	Joseph Dixon Co., Inc.
5. Dixon 78-143	$2.5\mu$	Lacquer	--	Joseph Dixon Co., Inc.
6. Dixon 120	$2.5\mu$	Water	30	Joseph Dixon Co., Inc.

(a) continuity, (b) resistance, and (c) uniformity. Such questions as vibration, rate of draw, wettability, roller direction, bake-out temperature speed and others listed in Table V were investigated in these preliminary studies using an experimental set-up similar to that shown in Figure 10. The filament sizing was removed with methylene chloride as part of the continuous process. Because of the fragility of the 1 mil filament and difficulty in dereeling it, draw speeds were limited to 40 feet per minute.

The results of these early experiments are shown in Table VI. The principal difficulty lay in achieving a uniform coating. Resistance fluctuations usually lay within 20 to 50 percent, but occasional jumps to infinite resistance showed that areas existed where no coating adhered. This was attributed at the time to inadequate removal of the hydrocarbon sizing from the filament. Later, as will be discussed below, it was found to be more or less characteristic of the filament dragging or being unevenly wiped by a roller.

A series of slides were dipped into various commercial graphite suspension mixtures to compare the surface obtained. From the standpoint of boron deposition, a glassy smooth surface would be most desirable. Since it is not a molecular process, as are CVD processes, a smooth coating is not obtained with graphite suspensions, although the possibility of mechanically

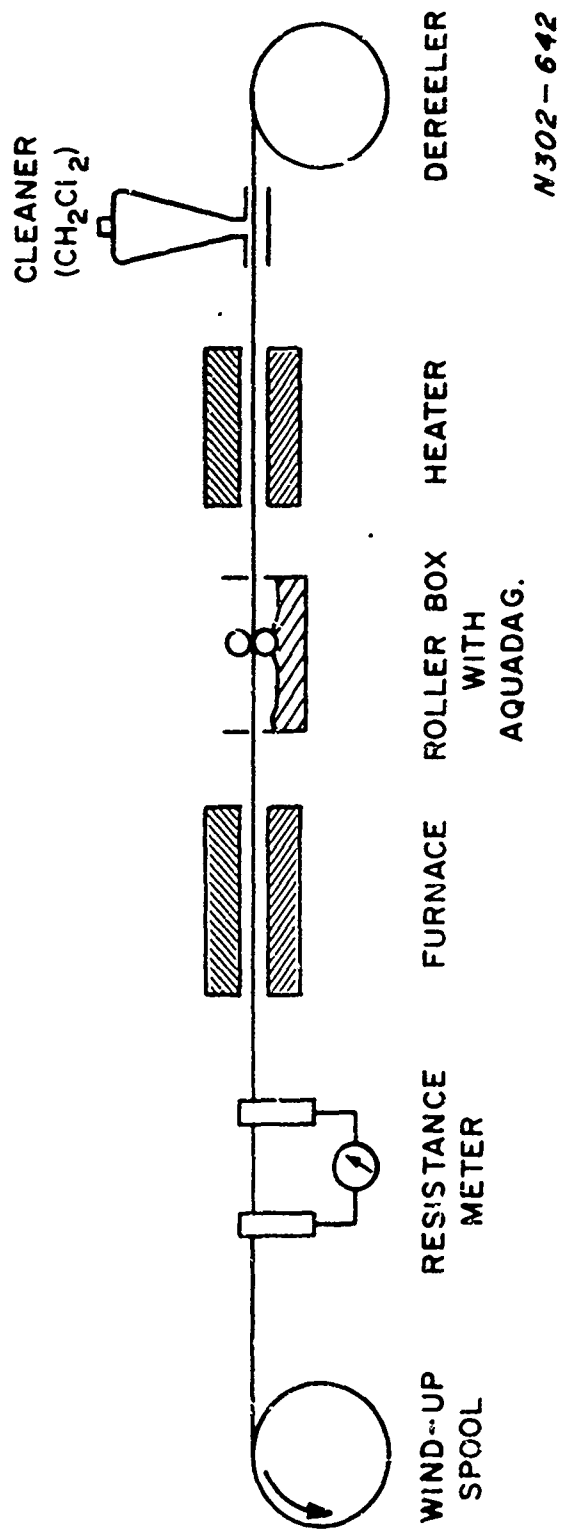


Figure 10. Experimental Set-Up for Coating Pre-Spooled S-Glass Filament

TABLE V  
VARIABLES IN GRAPHITE DISPERSION COATING PROCESS

1. Nature or source of dispersion (Aquadag, Graphilm, etc.)
2. Percent solids
3. Method of coating (e.g., roller, brush, etc.)
4. Type of surface on rollers (e.g., canvas, velveteen)
5. Filament speed
6. Coating roller speed and direction
7. Filament cleanliness (if sized)
8. Bake-out time
9. Bake-out temperature
10. Filament alignment
11. Vibration
12. Condition of dispersion (i.e., drying out, etc.)

TABLE VI  
PRELIMINARY CARBON COATING EXPERIMENT RESULTS USING  
PRE-SPOOLED S-GLASS

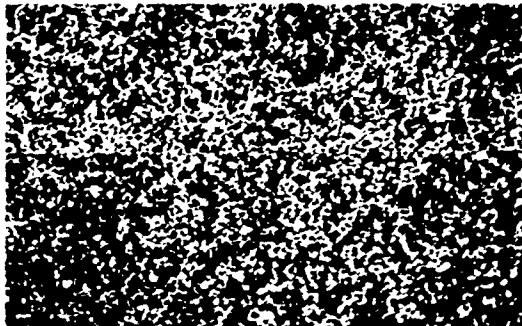
<u>Coating Agent</u>	<u>Filament Speed Ft/Min</u>	<u>Oven Temp</u>	<u>Comments</u>
Graphilm	100	400	Continuous Matte Finish, Gave Nodular Boron Deposit
RCA	100	400	Discontinuous
Aquadag	100	400	Discontinuous
Joseph Dixon 94-22 15 w/o	100	600	Poor Wetting - Tear-drops
Aquadag 15 w/o	200	600	Thin Spots
Aquadag 15 w/o	300	600	Thin Spots
Dixon	100	600	Discontinuous
Aquadag 15 w/o	100	600	Discontinuous
Aquadag 22 w/o	100	600	Smooth, Partially Continuous
Aquadag 18 w/o	100	600	Smooth, Continuous
Aquadag 18 w/o	200	600	Spotty
Aquadag 18 w/o	600	600	Spotty, Thin

polishing the surface after baking or of depositing additional carbon from a CVD process has yet to be explored. Figure 11 shows typical views of graphite suspension coatings on glass slides.

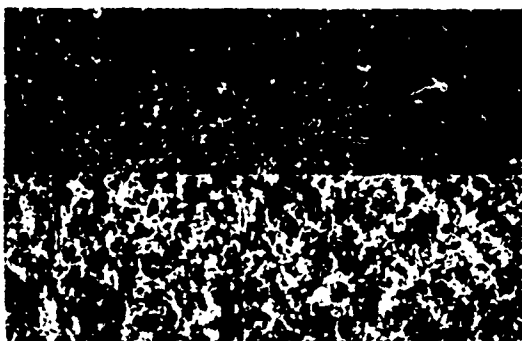
Inasmuch as the ultimate proof of the usefulness of this approach for coating a non-conductive glass filament is the performance of the coated filament as a deposition substrate, boron was deposited from diborane on S-glass filament coated from a mixture of Aquadag and Graphilm. During deposition, hot spots were observed to exist throughout the passage of the filament through the reactor. Uncoated areas caused the filament to break. Nevertheless a batch of this material was used to obtain 4.0 mil filament which had a maximum tensile strength of 260 ksi, a value comparable to that for boron on carbon-coated silica made in the same reactor under identical conditions during that period of time. The surface of the boron filament is of course affected by all of the asperities which existed at the substrate as a result of the graphite coating. Figures 12a and b are views of the surface and cross section of this filament. The rough nature of the graphite coating is clearly visible in the cross section in particular.

As the program progressed, the suspension coating techniques was integrated with the drawing of S-glass from the melt. Figure 13 shows the combined experimental apparatus schematically, while Figure 14 is a photograph of the assembly. Table VII lists the results of the experiments with this integrated set-up.

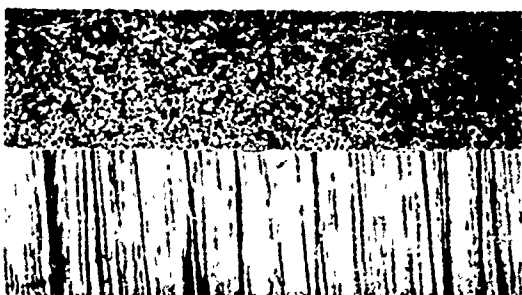
As the program progressed and the possibility of using the higher melting GE-177 glass arose, no further deposition studies were carried out with S-glass coated in this manner. However, when difficulties with the pyrolytic coating of GE-177 glass arose (see below), apparatus was again assembled for coating with graphite suspension as a means of providing conductive-cooled GE-177 glass for RF heated boron filament deposition. This time a double roller system was used, with a heat lamp between the first and second rollers, and a bake-out oven set at 600°C following the second roller. Less concentrated suspensions of Aquadag were prepared in a Waring Blender immediately prior to use; the filament draw was started



RCA Graphite  
Conductive Coating  
Top as Dipped  
Bottom Buffed  
(100X)



'Graphilm'  
(as Rec'd)  
Top as Dipped  
Bottom Buffed  
(100X)



'Aquadag'  
10 w/o Solids  
Top as Dipped  
Bottom Buffed  
(100X)

Figure 11. Appearance of Three Graphite Suspension-Type Coatings after Baking and after Lightly Buffing.



A



B

Figure 12. 4-mil Boron Deposited on S-Glass Coated from 22 w/o Graphite Aqueous Suspension.  
Top - Side View 600X  
Bottom - Cross Section 1210X



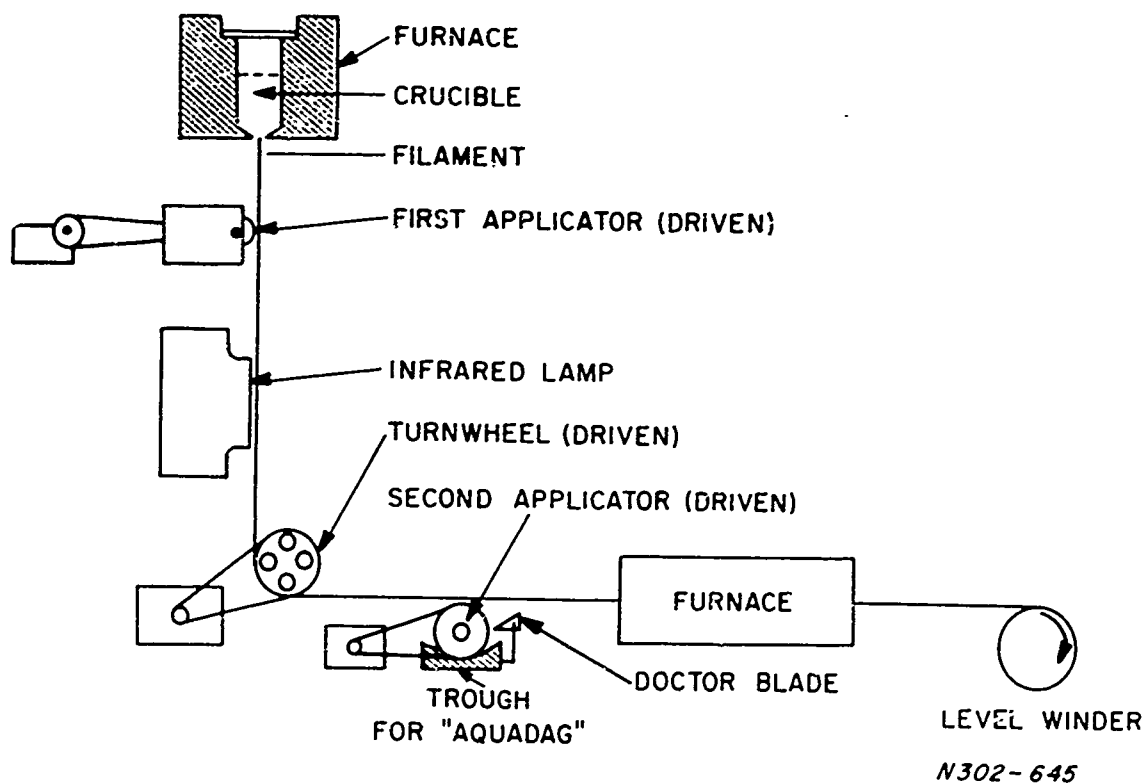


Figure 13. Schematic of Typical Integrated Glass Drawing and Aquadag Coating Arrangement

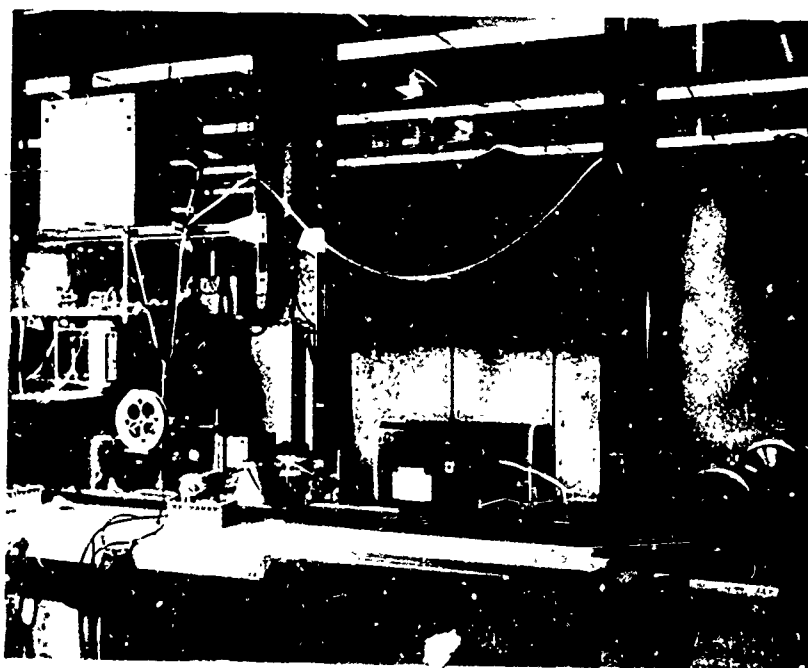


Figure 14. Integrated Drawing of S-1014 Glass - Coating with Colloidal Graphite

TABLE VII. RESUME' OF EXPERIMENTS WITH GRAPHITE DISPERSION COATING

Run No.	Filament	Speed Ft/Min	w/o Solids	No. Passes	Resist. (ohms)	Variation in Basic Process	Observation
47	Ferro, S-1014	40	22	1	$(10-20) \times 10^3$	Double roller 3/4" diam.	Very thin, spotty. No coat below 35 ft/min
48	Ferro, S-1014	10-50	9	1	$\infty$	Dil'n according to mfr.	1. Thin, spotty
49	Ferro, S-1014	46	9	1 2 3	$1.9 \times 10^6$ $0.8 \times 10^6$ $0.4 \times 10^6$	Three Passes	2. Areas of thinner coat
51	Ferro, S-1014	76 90	22 22	1 1	$4 \times 10^6$ $1.5 \times 10^6$	Single Pass Single Pass	3. Uniform
52	Ferro, S-1014	9	20	1	$(100-200) \times 10^3$ $3 \times 10^6$	(Alcohol Disp'n) (Alcohol Disp'n)	Alcohol base disp'n gave spotty, non uniform coats, with discontinuities
55	Pyrex, Task I	9-90	22	1	---		Very many breaks, very non-uniform
57	Ferro, S-1014	40	20	1	$3 \times 10^6$	Double Roller - Driven	Rel. Uniform
58			18	1	$(100-300) \times 10^3$	Diluted Aquadag	First pass-spotty
59			17	1	$10^6 - \infty$	Diluted Aquadag	Scraping, misalignment
59			17	2	1,000	Diluted Aquadag	Scraping, misalignment
60			15.7	1	$(80-150) \times 10^3$	Diluted Aquadag	Scraping, misalignment
61			14.7	1	$(200-400) \times 10^3$	Diluted Aquadag	Many breaks
62	S-Glass, Task I	40	14.7	1	400,000	Freshly Drawn	Many breaks, uneven coat
63	S-Glass, Task I	40	20	1	$(25-400) \times 10^3$	Alcohol Base Dispersion	
64	S-Glass, Task I	190-200	20	1	$(25-40) \times 10^3$	Velvet Roller 3/4" Diam.	Many breaks, vibration
65	S-Glass, Task I	190-200	20	1	$10^6$	Velvet Roller 3/4" Diam. Counter to Fil. Dir'n.	Fairly uniform

and the application rollers were rotated in a direction opposite to that of the filament travel (see Figure 13). Two compositions were used: a concentrated (20 v/o) and a dilute (12 v/o) mixture of Aquadag were applied with the double roller system during continuous drawing at 40 feet per minute. Relatively uniform coatings with resistances of 50,000 to 60,000 and 200,000 to 300,000 ohms per inch respectively were obtained with little difficulty. Variations in the latter case were infrequent and of minor size compared to experiments described earlier in which single roller applications were used with the integrated drawing and coating of S-glass. Several thousand feet of both materials were prepared for coating with boron using the RF heated deposition system described under Task III. Figure 15 shows views of both substrates while in Figure 16, typical sections of the two boron coated filaments are shown. Table VIII summarizes the test data obtained on boron filaments deposited in the RF reactor in various experiments using graphite coated GE-177 glass.

The use of RF described in Task III heating for this type of substrate was a considerable improvement over earlier experiments with graphite coated S-glass in which the resistance heating method was used. In the latter case, discontinuities, thin spots, and sudden changes in resistance either caused the filament to break or an unusually thick deposit to occur in one place. With RF heating however, a continuous circuit along the filament was not required. Bare places were coated by means of the heat generated in adjacent coated regions. The higher resistance coating mentioned above presented an almost uniform temperature profile as it entered the reactor despite variations in coating thickness, and the presence of lumps, bare streaks and spots, etc. on the substrate. Resistance changes at this high resistance level apparently had less influences than variations which occurred in the lower resistance filament. Here zones up to 3/4" long were apparent in which temperatures were different from the material before and after it. Diameters of boron filament prepared with this substrate were also less uniform. Nevertheless, the heating of this filament presented no noteworthy challenge.

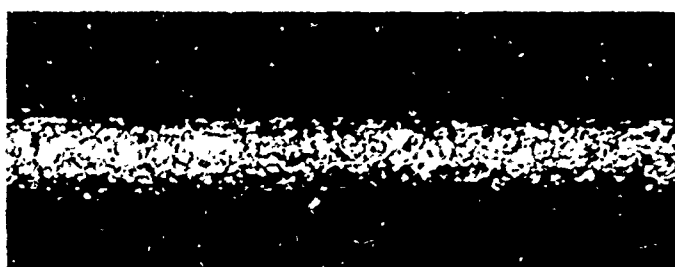
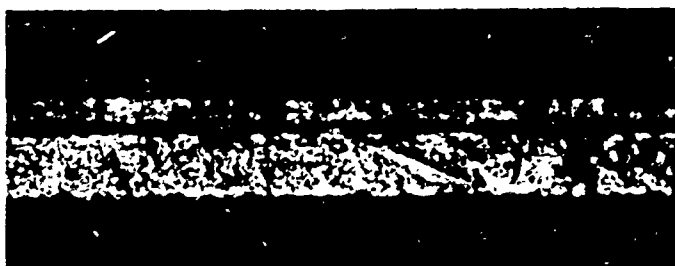
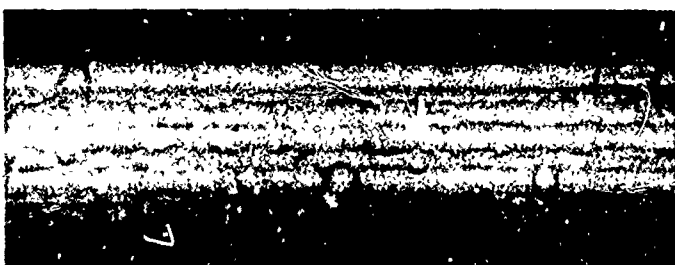


Figure 15. GE-177 Glass, Coated as Drawn with Graphite from Suspension



490X  
4.1 mils

Substrate Resist.  
200-300,000  $\Omega$ /in.



490X  
4.2 mils

Substrate Resist.  
50-60,000  $\Omega$ /in.

Figure 16. Boron Deposited on Graphite-Coated GE-177 Glass

TABLE VIII  
TENSILE STRENGTH OF BORON DEPOSITED ON GE-177 COATED  
WITH AQUADAG\*  
(1" Gage Length)

A. SUBSTRATE RESISTANCE 200-300,000 ohm/in.

Run No.	<u>1</u>	<u>2</u>	<u>3</u>
	250 Ksi	258 Ksi	268 Ksi
	280	220	231
	280	250	285
	280	250	251
	205	265	276
	295	250	226
	<u>242</u>	295	243
Avg.	262	280	243
Diam.	4.1 mils	258	218
		<u>288</u>	<u>201</u>
		Avg. 261	Avg. 242
		Diam. 4.1 mil	Diam. 3.9 mils

B. SUBSTRATE RESISTANCE 30-40,000 ohm/in.

	<u>1</u>	<u>2</u>
	167 Ksi	159 Ksi
	96	223
	183	151
	239	231
	239	239
	254	207
	<u>231</u>	199
Avg.	201	<u>223</u>
		Avg. 204
		Diam. 4.0 mils

\*Tests were made on consecutive 4" long specimens.

It should be also pointed out that the experiments conducted with this filament were preliminary and were not therefore the ultimate in process development. The uniformity in tensile strength characteristic of the RF heating process filament persisted in filament made with the graphite coated substrate in spite of nodules, bare streaks and various other surface asperities noticeable on the boron surface (Figure 16).

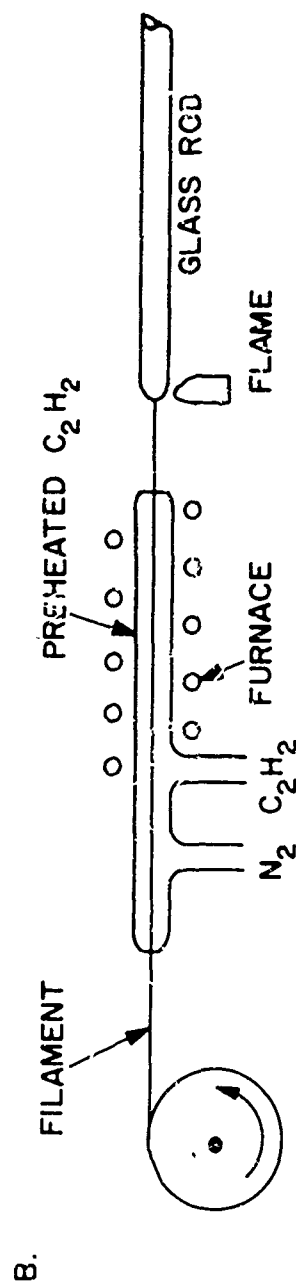
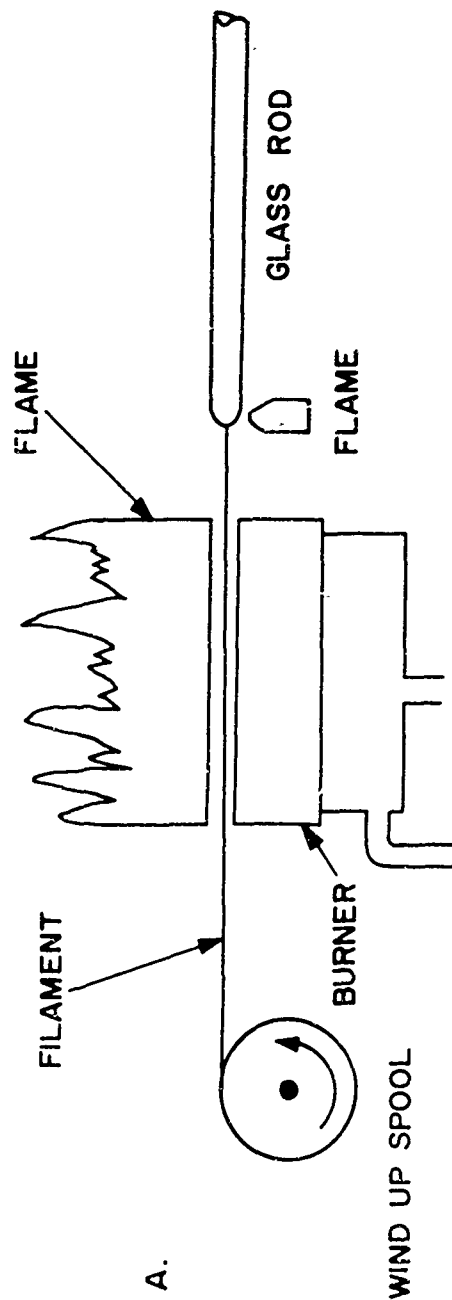
#### D. PYROLYSIS AT MODERATE TEMPERATURES: CARBON COATING

Providing that sufficient thermal energy can be applied to the filament surface without its breaking, the decomposition of hydrocarbons to carbon and hydrogen can be considered as a candidate reaction for forming a conductive coating of carbon on a freshly formed filament surface. For example, the decomposition of acetylene occurs at around  $600^{\circ}\text{C}$  at a measurable rate which becomes explosive, or spontaneously sooty at around  $850^{\circ}\text{C}$ . At the lower temperatures however, the reaction products are not well characterized although considerable polymerization is known to occur, leading to formation of higher molecular weight solids<sup>(5)</sup>. Nevertheless, sufficient carbon can be formed to cause a conductive layer to adhere to a filament.

Catalytic methods, such as the addition of boron trichloride to the gas feed can also increase the rate at lower temperatures.

##### 1. Electrical Preheating

In order to carry out the decomposition of small hydrocarbon molecule at the surface of a hot filament immediately after drawing from a rod or melt, it is necessary to have the filament enter a reactor, containing the hydrocarbon mixture while it still retains some heat. The general experimental arrangement shown in Figure 17B was used for this portion of the work. It consists of a tube, externally heated through which the filament and hydrocarbon gas mixture pass in opposing directions. The latter is preheated by the external furnace while the former retains some of the heat used in drawing. The preheater must be kept below the temperature at which the gas spontaneously decomposes and deposits on the walls; the filament on the other hand must cool sufficiently to finish elongating, but must remain hot enough to provide a surface for reaction. Various tube designs were used to provide longer preheat zones, to permit boron trichloride and acetylene to be introduced separately, and to permit the offgases to burn at a point away from that at which the filament was being introduced. Critical factors in the experiment were preheater temperature, filament draw speed, distance between the filament drawing tip and the entrance to the reactor, and gas feed rate.



N302-757

Figure 17. Experimental Arrangements for Drawing and Pyrolytic Carbon Coating.

Thermal decomposition reactions as a route to a carbon conductive coating were used with GE-177 and Corning 1716 glass, both of which have sufficiently high drawing temperatures to permit some of the heat to remain in the drawn filament long enough to be of value in the coating process. S-glass on the other hand is drawn at lower temperatures and was not found to be useful for this purpose. In all of these cases, despite fairly high softening points compared to borosilicate glasses for example, the filament strength in the range of the decomposition reaction is too low to allow the drawn and cooled filament to be reheated, as is permissible with quartz and Vycor for example.

Table IX summarizes a series of experiments using GE-177 glass for the most part as the substrate, with occasional results for Vycor as checkpoints. The process at its most efficient gave conductive coatings between 0.5 and 20 megohms per inch, depending on diameter. Geometric limitations permitted the loss of heat from the filament prior to its entry into the coating reactor, accounting for higher resistances. In some cases, particularly when the flow of boron trichloride was high along with high preheater temperature, sooty particles were found on the filament surface. These were rather readily removed by wiping, without affecting pyrolytic coating. In other cases, where preheater temperature was low, or where no boron trichloride was used, the filament had a brownish non-conductive coating, probably polymeric in nature.

## 2. Flame Preheating

Pyrolytic carbon coatings were deposited on GE-177 and Corning 1716 glass, as well as on silica and Vycor filaments after each had been drawn from a rod using the apparatus depicted in Figure 17A. In this set-up, the filament is drawn from the hot rod as close to the burner flame as possible. Indeed, the flame rested on the top of the burner. The latter was a water cooled circular three-inch porous plug diffusion burner having a 1/2 inch annular cooling ring. The filament was drawn across the face of the burner, beneath the flame in such a way that it spent a minimum of time traversing the distance between the hot point and the gas zone. The gases fed to the



TABLE IX  
PYROLYTIC CARBON COATING ON GLASS EXPERIMENTS

Date	Page	Glass	Draw Speed ft/min	Hydrocarbon	Flow Rate cc/min	BCl <sub>3</sub> Rate cc/min	Preheater Temp. °C	Flame Distance inches	Diam. mils.	Resist. K-ohm/in.
4" HOT ZONE										
12/1	56	Vycor	60	C <sub>2</sub> H <sub>2</sub>	200	---	700	1	3-4	50-20
12/5	58	GE-177 C-1716	---	C <sub>2</sub> H <sub>2</sub>	200	---	700-750	1 1/2-2	---	*
12/6	60	Vycor	60	C <sub>2</sub> H <sub>2</sub>	200	---	750	3/4	1.4-2.1	500-750
12/7	61	GE-177	500	C <sub>2</sub> H <sub>2</sub>	100	---	700	2	1.2-1.5	*
		GE-177	500	C <sub>2</sub> H <sub>2</sub>	100	---	700-900	1 3/4	1.2-1.5	*
12/8	62	GE-177	500	C <sub>2</sub> H <sub>2</sub>	100	---	950-1000	3/4	---	*
12" HOT ZONE										
12/14	66	Vycor	500	C <sub>2</sub> H <sub>2</sub>	100	---	700	3/4	1.9-2.1	2000
		Vycor	500	C <sub>2</sub> H <sub>2</sub>	100	---	900	3/4	1.7-2.1	500-650
12/15	67	GE-177	400-500	C <sub>2</sub> H <sub>2</sub>	60-120	---	900-950	1 3/4	---	*
12/19	69	GE-177	400	C <sub>2</sub> H <sub>2</sub>	60	6	990	1 3/4	---	*
12/20	71	GE-177	400	C <sub>2</sub> H <sub>2</sub>	60	6	950	1 3/4	1.5-1.7	2000
1/3	75	GE-177	300	C <sub>2</sub> H <sub>2</sub>	60	6	950	1 1/2	2.6	700-1200
1/4	76	Vycor	300	C <sub>2</sub> H <sub>2</sub>	60	6	910	3/4	1.3-1.5	700
1/12	91	GE-177	300	C <sub>2</sub> H <sub>2</sub>	60	6	950	1 1/2	1.5-2.0	1000-20,000
1/24	88	GE-177	300	C <sub>3</sub> H <sub>2</sub>	60	3	950	1 1/2	1.9	7000-15,000
1/29	90	GE-177	200	C <sub>3</sub> H <sub>2</sub>	60	---	900-950	1/2	1.5-2.0	*
1/30	91	GE-177	300	C <sub>3</sub> H <sub>2</sub>	60	3	900	1/2	1.5-2.0	3000-5000
2/7	93	GE-177	300	C <sub>3</sub> H <sub>2</sub>	20-30	3	950	1/2	---	7000-40,000
SEPARATED FLOW REACTOR										
2/14	95	GE-177	200	C <sub>2</sub> H <sub>2</sub>	60	2	950	1/2	2.1	2000-15,000
		GE-177	300	C <sub>2</sub> H <sub>2</sub>	60	2	950	1/2	2/1	3000-30,000
2/20	98	GE-177	200	C <sub>2</sub> H <sub>2</sub>	60	2	950	1/2	1/2	1000-7000

furnace consisted of acetylene or propane mixed with oxygen. Under the right feed conditions, the flame hovered about 1/4 inch above the face of the burner, reflecting heat into this region and thus preheating the gas.

The critical aspect of the arrangement was to prevent heat loss from the filament prior to reaching the preheated gas zone. Factors affecting this were drawing speed and filament diameter which work in opposing directions to this end. At higher speeds, the filament was exposed to low temperature regions for a shorter time, but the diameter was smaller and the amount of heat carried along was less. In preliminary experiments using Vycor and quartz rod to establish flame conditions, little difficulty was encountered in obtaining continuous adherent coatings of pyrolytic carbon which were electrically conducting. For example, using a mixture of acetylene (1400 cc/min.), oxygen (950 cc/min.) and nitrogen (3655 cc/min.) in the burner, coated Vycor of 1.9 mils was drawn having an average resistance of 300-600 Kohms/in. Drawing speeds up to 600 feet per minute were used.

Further experiments using Corning 1716 and GE-177 glasses established that the lower drawing temperature compared to Vycor and silica prevented the achievement of a conductive coating on filaments less than about 3 to 4 mils in diameter. Below this limit insufficient heat was available to crack the hydrocarbon, while attempts to preheat the filament or to increase the amount of heat reflected from the flame to the burner top resulted in melting the filament. However, larger filaments were readily coated with a silvery lustrous carbon layer with electrical resistances between 100 and 500 Kohms/in. No crazing or checking was observed which would indicate deterioration of the glass during the coating process, nor were the films easily removed. In view of the diameter requirement for boron filaments (1 mil), work with flame coating in this manner was discontinued until the resistance heated glass drawing bushing for use with 177 glass in Task I was ready.

It should be noted that the mechanism of deposition in this case differs from that encountered in conventional flame deposition. In the latter case,

carbon, formed by incomplete combustion of the fuel mixture, rises to the upper portion of the flame zone where it encounters the relatively cool filament surface as it is being drawn through this region. It condenses as a pyrolytic deposit on this surface. In the work carried out on this program, the flame serves only as a heat source to radiate thermal energy into the gas mixture entering the flame region from below. A sufficiently hot object entering this region promotes thermal decomposition of the hydrocarbon molecules at the surface, with carbon as the least volatile product. If the entering surface is not hot enough, no reaction and consequently no deposition occurs.

### 3. Integrated Melt Drawing and Pyrolytic Coating

A difficulty experienced with filament drawn from the rod and coated in the pyrolysis reactor lay in the resistance variation along the filament. Heating methods exist which can be used with filament resistances up to about 10 megohms per inch. However, variations cause problems with any heating system. A survey was made on filament prepared in one of the better experiments shown in Table IX to determine if the resistance variation followed that of diameter. As Table X shows, this was the case. The glass rod used for the drawing was not of optical quality. Diameter variations, bubbles and splices were encountered during the drawing. In drawing from the melt, these

TABLE X  
TYPICAL VARIATION IN FILAMENT DIAMETER  
AND COATING RESISTANCE

<u>Diameter</u>	<u>Resistance (meg ohm/in.)</u>
1.8	35
3.5	7
2.8	8.5
2.85	7.5
3.1	10
2.8	14
3.3	15
3.1	20
2.8	7
2.7	10

difficulties would not be expected. Consequently, when the drawing of GE-177 became routine a pyrolytic coating reactor was designed and tried.

The thermal decomposition reaction apparatus was integrated with the bushing for the drawing of GE-177 glass from the melt in the manner shown in Figure 18. The experimental coating reactor for the gas decomposition is shown schematically in Figure 19. Figure 20 is a modification of the reactor shown in Figure 19, which was designed to prevent excessive sooting of the hydrocarbon as a result of exposure to the infrared radiation around the bottom of the glass drawing bushing. It consisted of a tube similar in design to that used in rod drawing experiments, modified to permit the orifice to fit closely to the gas containing tube and to prevent the exhaust gases from contacting the bushing directly. The first of these two arrangements was sealed to the bottom of the furnace with silica cement and an asbestos gasket, formed in place. The thinner tube was merely slipped into place within the larger tube and clamped there. In neither case was glass drawing hindered, although visibility was poor. The use of the preheater furnace had a marked effect on the bushing temperature, and necessitated considerable adjustment of the melting furnace controls until equilibrium was reached.

Despite the precautions taken to prevent excessive sooting around the heated orifice, it occurred with all gas mixtures tried. These consisted of: acetylene-boron trichloride, acetylene, acetylene-nitrogen, propane, propane-boron trichloride, propane-nitrogen. Excessive sooting, of course, caused the filament to be useless for deposition while a lesser degree of sooting generated a carbon film in the vicinity of the bushing which lowered the orifice temperature and caused the filament to break.

The principal difficulty with this design lay in the fact that the hydrocarbon gas could rise up through a high radiation zone below the orifice. Methods to prevent this by baffling with a hot gas jet, or by changing the direction of the draw from vertical to horizontal would not necessarily help the situation unless radiation baffles could be provided.

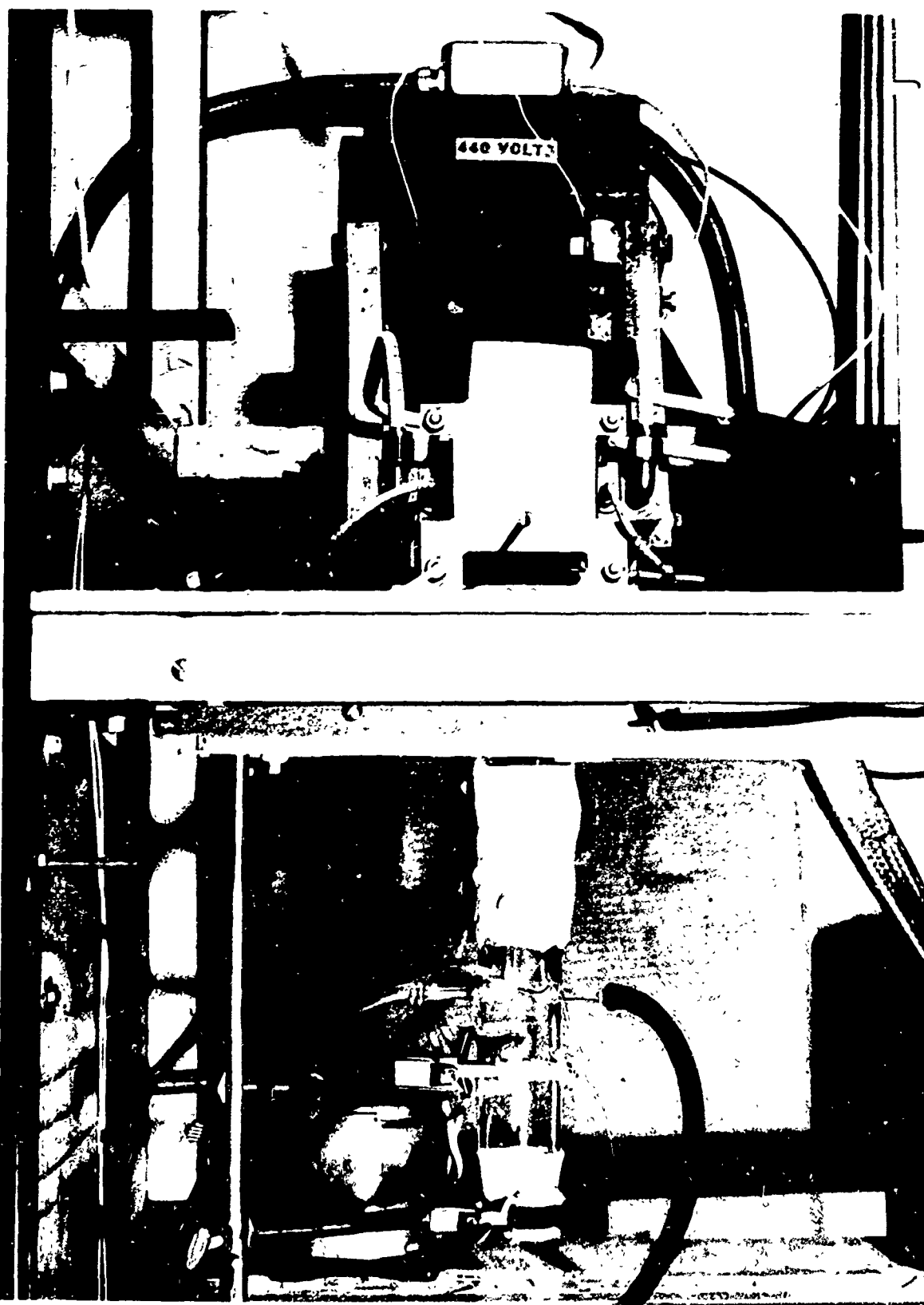
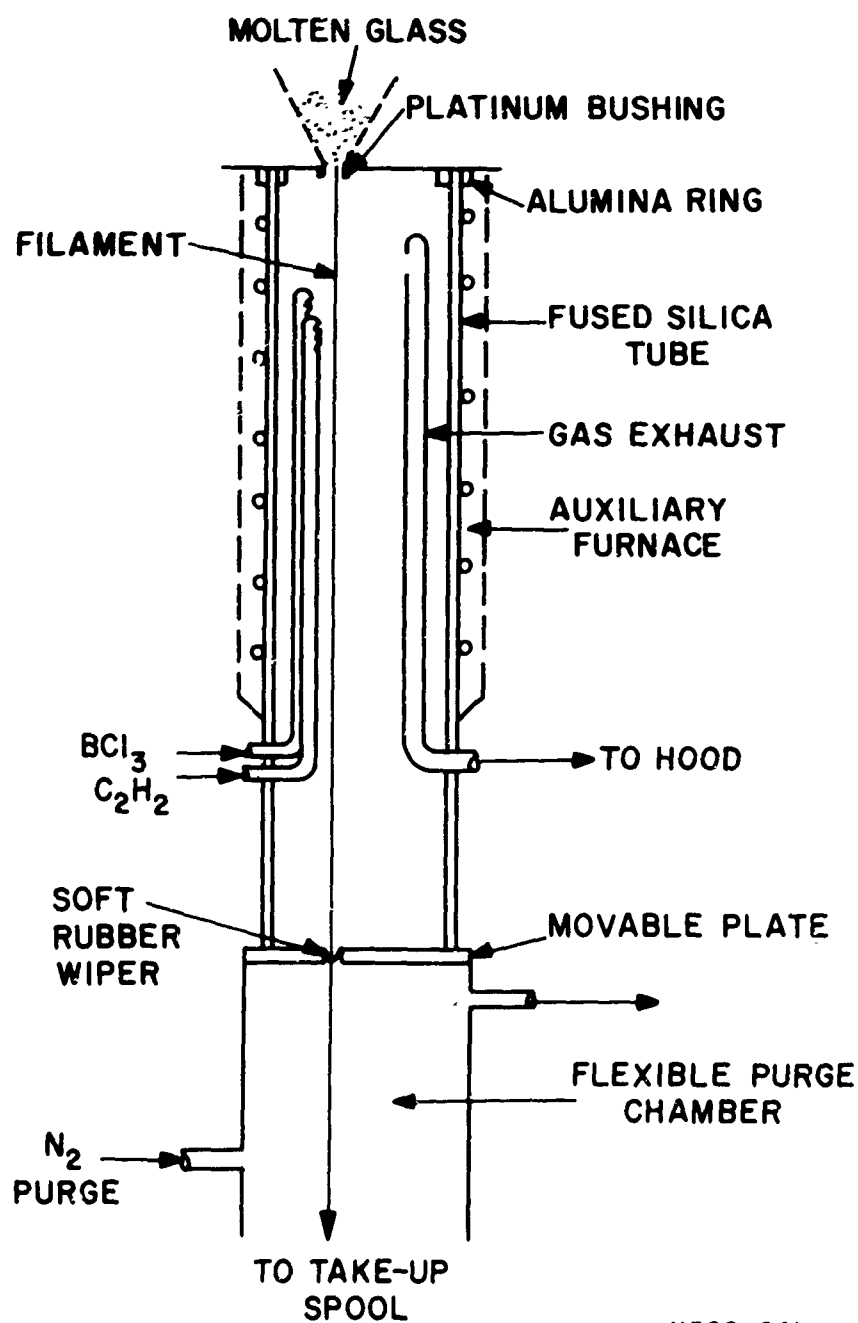
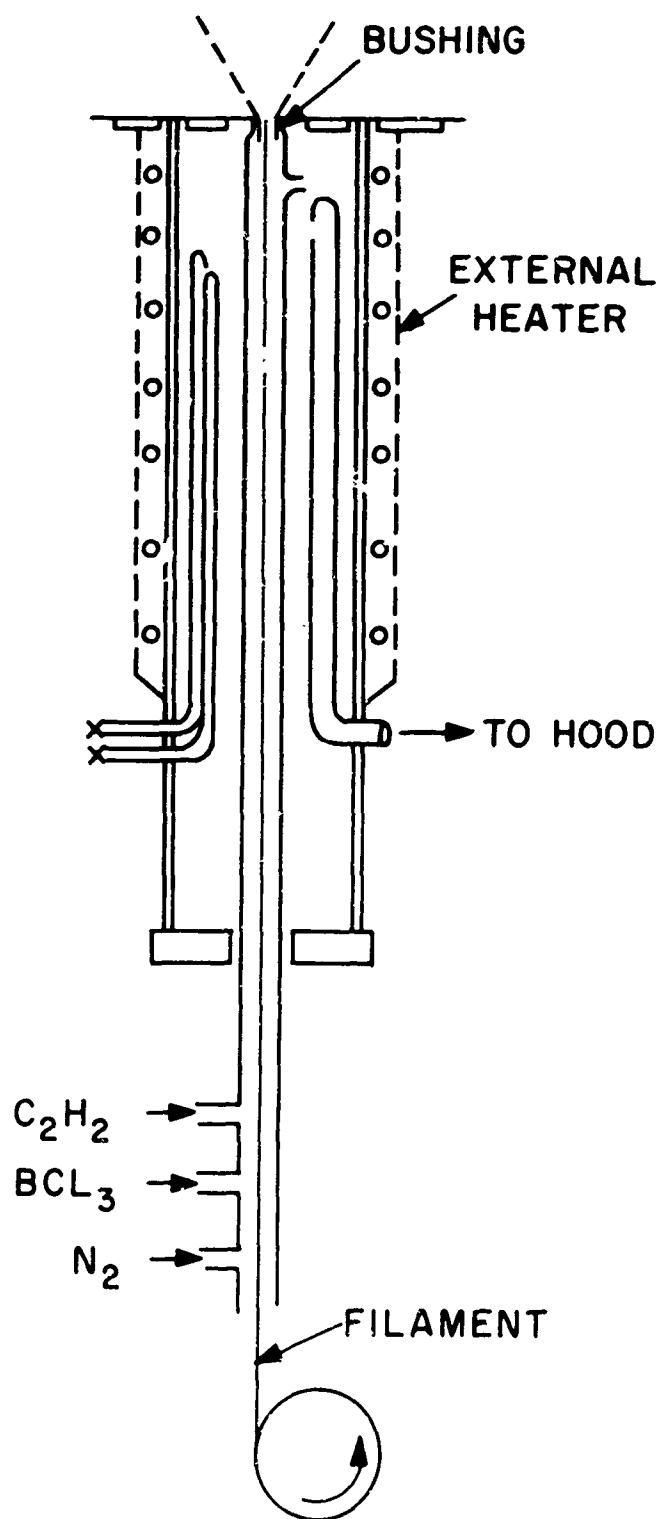


Figure 18. Close-up of Pyrolytic Coating Chamber in Position (Purge Chamber not Shown) Under Glass Drawing Bushing.



N302-841

Figure 19. Schematic of Thermal Decomposition Reactor for Filament Drawn from Bushing.



N302-897

Figure 20. Modified Thermal Decomposition Reactor for Applying a Pyrolytic Carbon Coating on Glass Monofilament

## SECTION IV

### TASK III - FILAMENT HEATING METHODS

Objective: To develop a non-mercury electrode method of heating the substrate and boron filament.

#### A. BACKGROUND

The broad effort which has been sustained over the past years in the development of boron filament has as its ultimate goal the large scale production of material in an economical manner. The purpose of this overall program was to develop such a process based on integrated drawing, coating, and deposition steps. This task has as its particular goal the development of a method of heating the filament during boron deposition that fills the requirements of an industrial process, i. e., low maintenance and cost, reliability and (preferably) simplicity. Historically, boron filaments, on both tungsten and silica cores have been prepared in reactors that are substantially the same as laboratory reactors. Contact between the electrical source of power and the filament has been made using variations of a mercury standpipe contact, in which the filament passes through a pool of mercury connected to the circuitry. While it has been successful to a large extent in the relatively limited production efforts mounted thus far, there are serious drawbacks to this approach in a high-speed, large-scale production system. For example, the loss of heat to the mercury pools and their temperature rise, even at relatively low draw speeds of 10-20 feet per minute, is sufficient to require replacement of the mercury at fairly short time intervals. Not only does the loss of heat represent a power waste, but the heated surfaces of the mercury and its container are possible hydride polymerization sites (see Task IV). The loss of the surface tension of mercury at high speeds is another possibility which makes its replacement desirable, as is also the possible contamination of the filament and introduction of flaws by mercury.

The effort in this task has been directed toward finding a suitable method for heating the filament which does not have the drawbacks of the mercury electrode and which would be practical in a manufacturing sense.



The methods chosen for bringing the substrate to deposition temperature fall into two categories - direct and indirect. The former consisted of various types of solid contact arrangements between the filament and electrical circuits. Design considerations included minimum tension and friction, good heat transfer, low junction potential and constant contact. The latter approaches, which proved to be more successful, were based on the use of microwave and radio frequency interaction with the filament to generate a current in the conducting layer.

## B. DIRECT CONTACT METHODS

### 1. Solid Contacts, Moving and Stationary

At the outset of the program, a basic reactor design was envisioned in which the filament would be drawn over a series of rotating electrically conducting wheels or pulleys, or sliding contacts, while diborane was passed over the heated portions of the filament between the contacts. This concept is illustrated in Figure 21 in which pulleys are depicted, although sliding contacts or electrical preheater units could be substituted. It was anticipated that such an enclosure would serve as an apparatus for practical testing of the various types of contact, in the deposition environment.

The transfer of electric power from one solid component to another embraces a host of variables most of which are associated with (a) the level and type of power and (b) the geometry and properties of the contacts. A third set of variables covers the atmosphere in which the contact operates and is usually moist or dry air, or inert. In the present case however, it is a highly sensitive and reactive gas of varying composition at low pressure which presents an additional area of concern. Much of the theory which has been developed in this field applies to situations which are somewhat simpler and in which more degrees of freedom are available to the designer.<sup>(6)</sup> An even larger body of practical experience is therefore of more immediate assistance. Combining both theory and past experience with contacts, as well as with the nature of the process at hand, led to identification of a number of key factors which were evaluated experimentally. These were

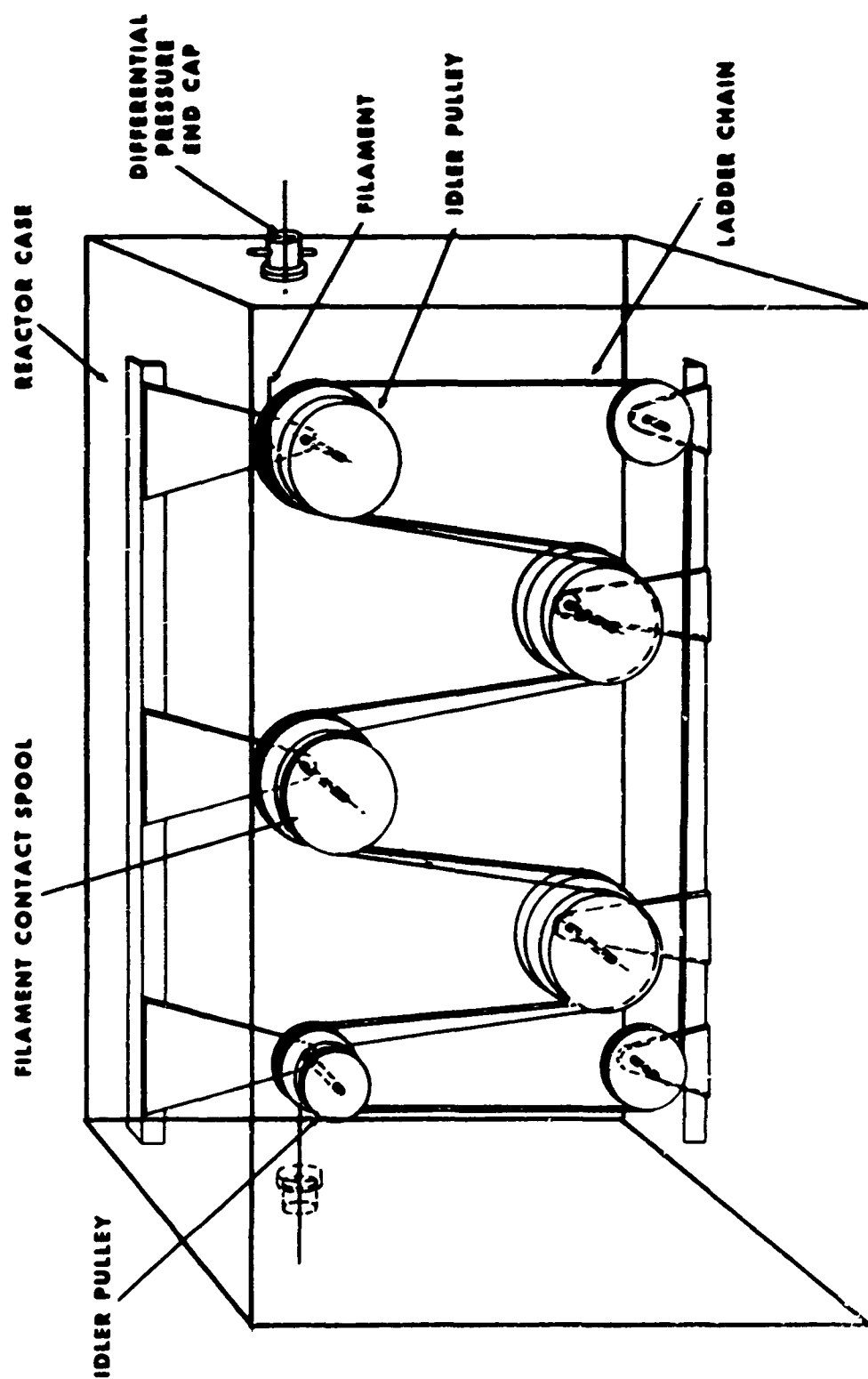


Figure 21. Apparatus for Testing High Speed Filament Processing.

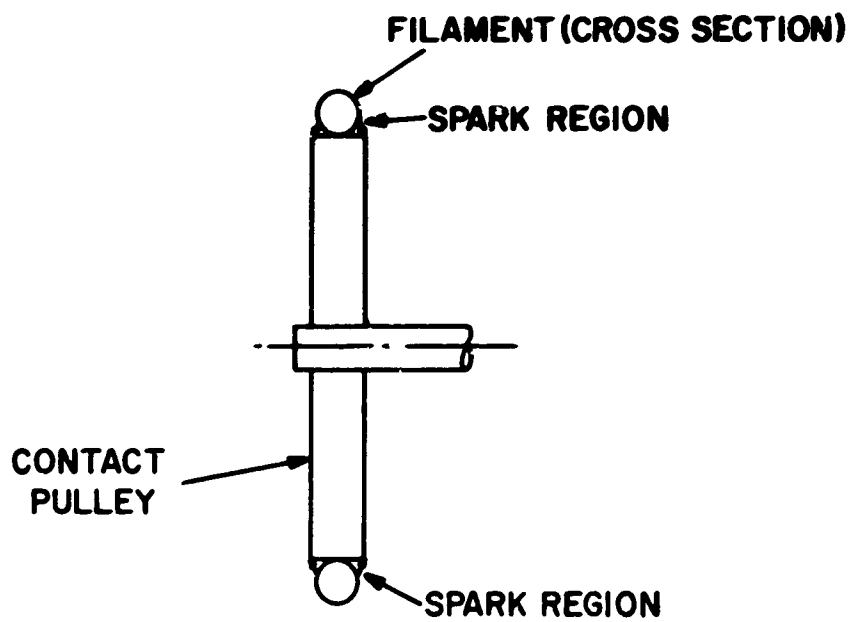
- 1) arcing, sparking and discharge
- 2) vibration and tension effects
- 3) thermal effects on the chemistry of diborane at the contact
- 4) geometric effects on the filament.

Arcing and discharge with subsequent breaking of the filament was considered to be the most severely limiting problem considering the anticipated speed of drawing, i. e. up to 1000 ft. /min., and the geometry of the filament with respect to the contact surface. Figure 22 illustrates several regions in the vicinity of the filament where arcing could be a problem with a design limited to line contact at best, between the filament surface and the conducting surface, exemplified by a wheel in this case. The probability of such occurrences is, of course, increased by the required operation at high voltages in a low pressure reactive atmosphere. Excessive local heating for short periods of time (micro-milliseconds) is known to occur when a spark or drawn arc is generated over short distances ( $10^{-4}$  cm). On the whole this was initially the most difficult technical problem in the program; however, the development of an RF heating method has not only solved the problem but provided a major advance to the filament field.

Contact Design - A variety of electrical contacts were designed and built for testing their ability to make continuous contact with a moving filament of high resistance without causing it to break either through sparking or through causing mechanical failure. These contacts were basically sliding or rolling, with various methods for maintaining contact and the nature of the contact surface constituting the principle differences between them. Referring to Figures 23, 24 and 25, these will be discussed together with experimental results obtained in tests with a carbon coated fused silica filament in an inert, dry atmosphere.

Floating Contact - Anvil Contact - Two designs were tested which are shown in Figure 23a and Figure 24. The former had a spring loaded float pressing upward against an inert, non-conducting anvil. Mercury was substituted for the spring, which lead to the design in Figure 24 in which

# **LATERALLY FROM FILAMENT**



# **LONGITUDINALLY BETWEEN FILAMENT & CONTACT PULLEY**

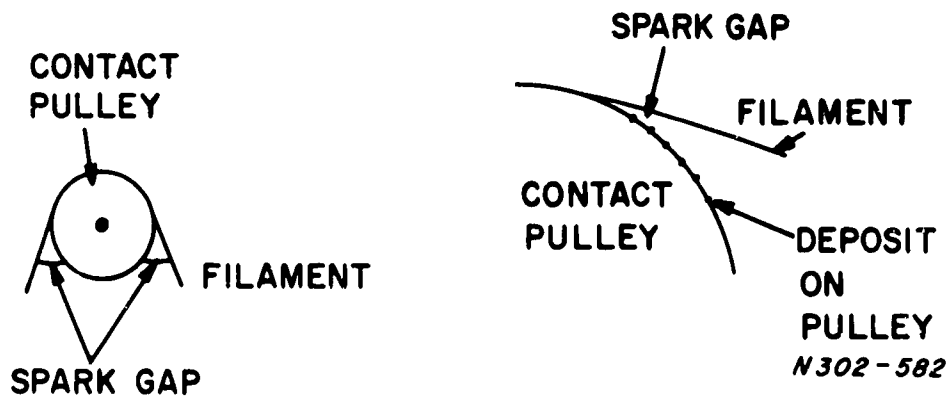
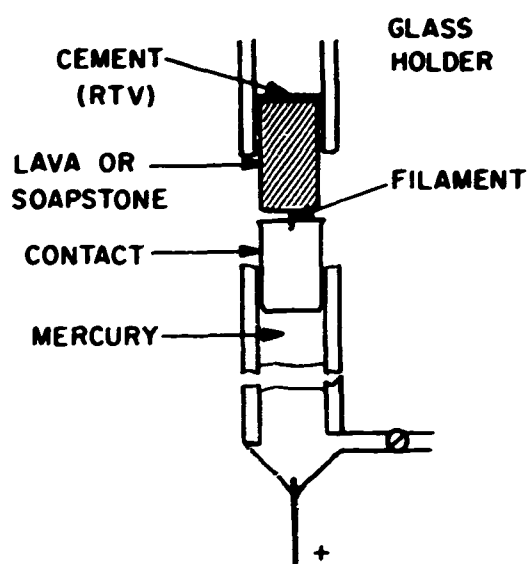
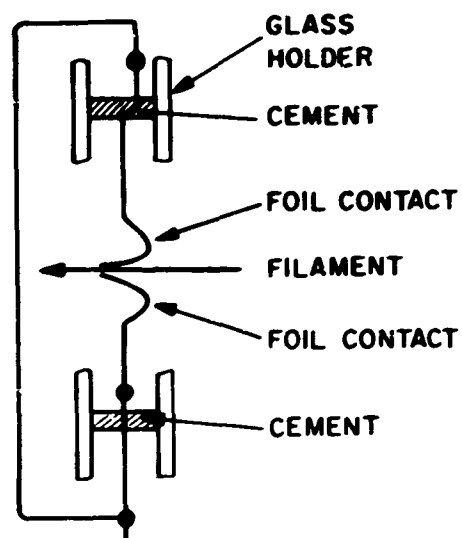


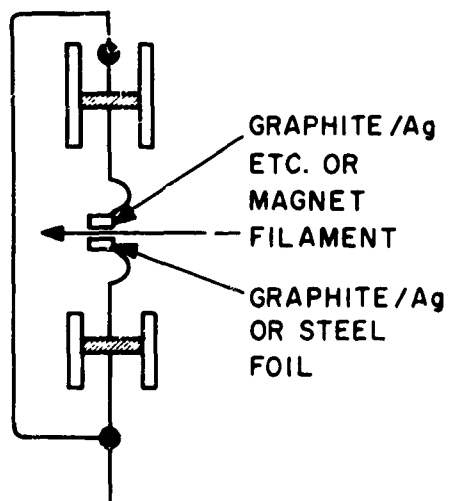
Figure 22. Potential Arcing and Sparking Sites on Dry Contacts.



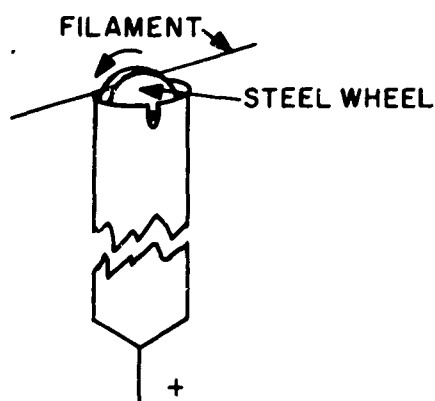
a. FLOATING CONTACT-ANVIL CONTACT



b. SPRING-CLIP CONTACT (1)



c. SPRING-CLIP CONTACT (2)  
WITH GRAPHITE CONTACT OR  
MAGNETIC GRIP



d. FREELY SPINNING CONTACT  
WHEEL

N302-643A

Figure 23. Various Types of Electrical Contacts

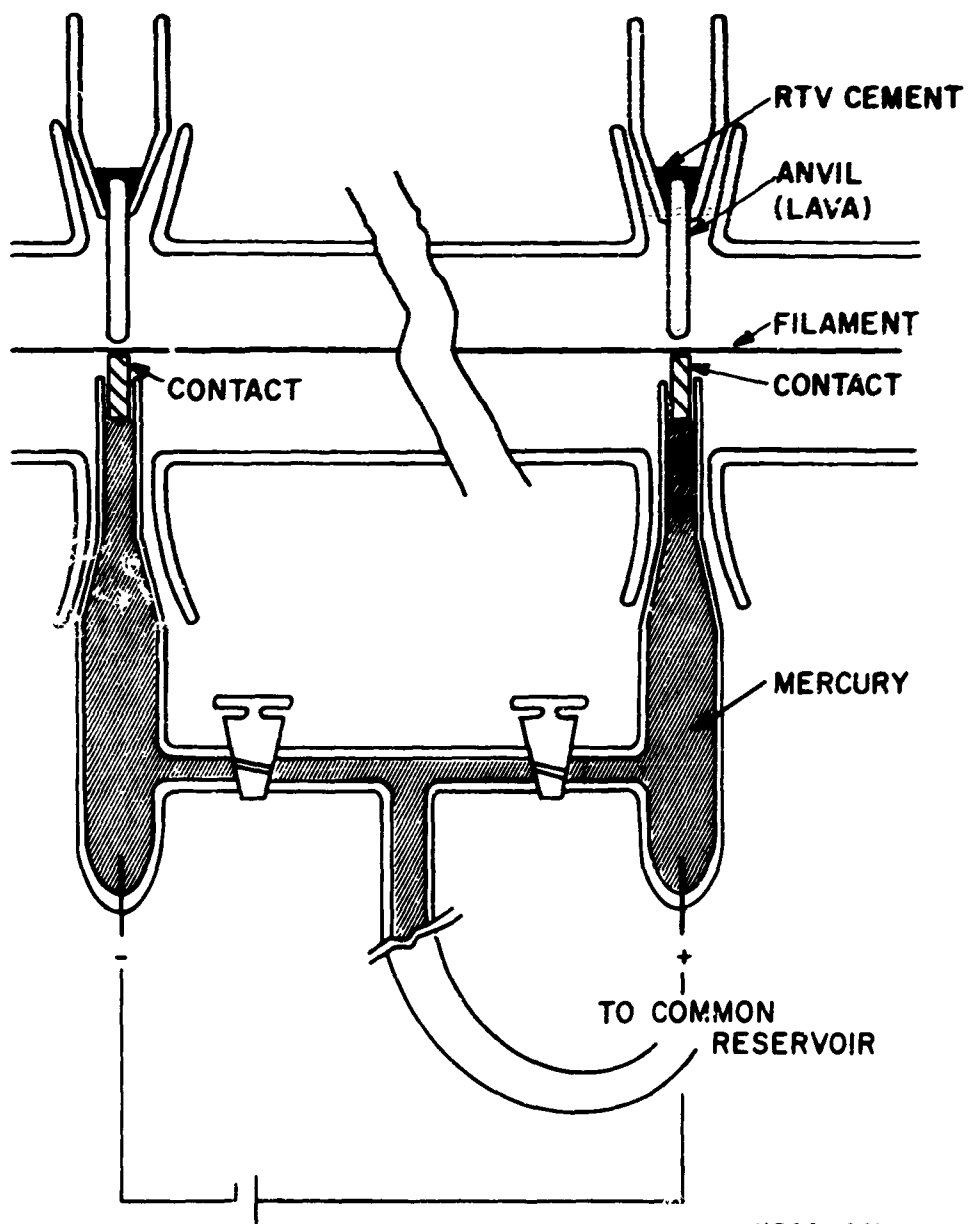
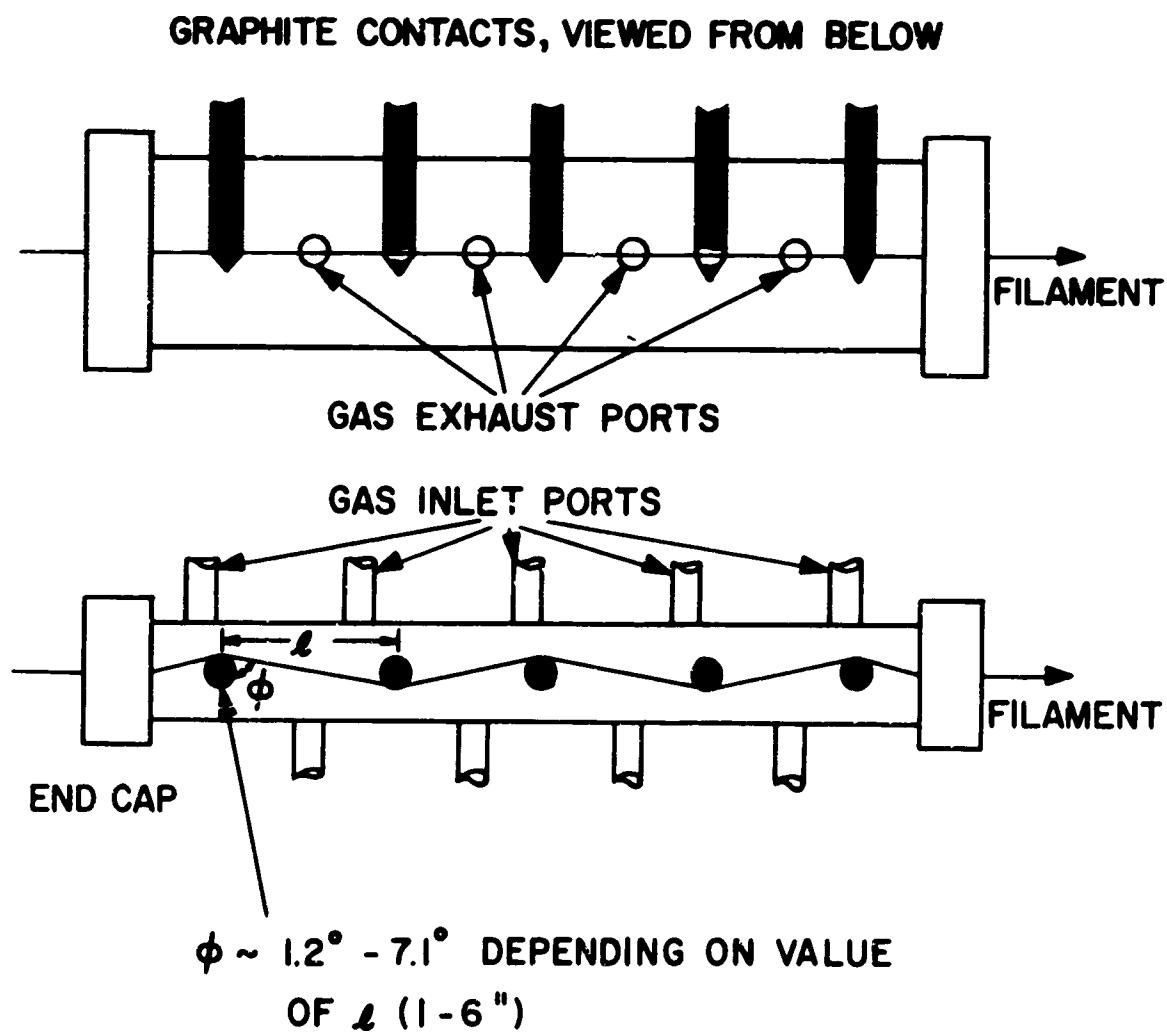


Figure 24. Floating Contact-Anvil System.



*N 302-756*

Figure 25. Schematic of Graphite Rod Contact which Produced Curved Filament.

the tension against the filament could be varied by the head of mercury applied to the floating contact. Such cushioning was also provided by allowing the contact to float on the mercury meniscus rather than by forcing it against the anvil.

A number of different contact materials were used for making the lower portion of the contact. These included silver-graphite composites (high altitude aircraft brush material, Speer Carbon Co.) a molybdenum disulfide-graphite composite (General Electric Company), a dense soft graphite (annealed pyrolytic graphite), brass, and bronze. The contacts were sealed into a cylindrical tube so that a filament could be drawn through end-plugs and between the contacts while a low flow of dry nitrogen was maintained in the tube. Carbon-coated fused silica filament (resistance of 250,000 ohms/in.) was used together with a neon light high voltage low current transformer attached to the output of a Variac. The filament was dereeled from a friction brake controlled spool and wound up on a spool driven at various speeds up to about 40 feet per minute.

The results were similar for all of the designs based on this general concept. Arcing and sparking occurred with increasing frequency as the draw speed was increased until parting of the filament occurred. When the pressure against the filament was increased, breaking occurred at lower speeds. No one contact material appeared to be preferable inasmuch as the same phenomenon occurred with all of them.

## 2. Spring Clip Contacts

The principal drawback to the hammer-anvil contact appeared to be the excessive amount of pressure to ensure contact with the filament. A lighter arrangement as designed using springy metal foil in the manner shown in Figure 23b and c. In Figure 23b, the upper and lower portions of the contact are in the circuit to prevent arcing over from part to the other. No contact surface other than the metal itself was provided. A variation in which a somewhat more positive pressure was provided to hold the filament in place is shown in Figure 23c. A small magnet held the lower part of the contact made of steel foil against the upper part on which the magnet was



mounted. Thin sheets of various contact materials were cemented to the opposing faces of the springs.

Tests were conducted with this arrangement in the apparatus that was described above. Somewhat higher speeds (40 ft/min.) were achieved for longer period of time (up to 2 minutes of continuous running) before arcing and burnout occurred. The immediate cause of the sparking was the collection of particles of carbon on the downstream clip. None appeared on the upstream contact, so that it may be deduced that heating the filament caused the coating to loosen in some manner so that it abraded off. During the period while the filament was heated and being drawn through the electrode, it remained radiant, so that it may be presumed that heat was also transferred to the electrode. In the event that this design should be used in deposition studies, it would be necessary to prevent deposition from occurring on the electrode and fouling the conducting surfaces.

### 3. Roller Contacts

A freely spinning steel roller, mounted as shown in Figure 23d was used for tests similar to those described above. This was perhaps the most successful direct contact design tried, although the filament eventually sparked and broke after a few minutes of running at 40 feet per min. At this speed the dereeling device became difficult to control and considerable jerking and vibration occurred as a result, which made further evaluation difficult. As it passed over the roller at 40 feet per minute, the filament carried heat to a distance of about one and a half to two inches beyond the second roller. Here again it would be necessary to prevent the roller from becoming hot particularly in the borane system.

### 4. Sliding Contacts

Figure 25 shows the apparatus used to test a series of graphite rods with slots cut in the ends to accommodate a filament being drawn across the rods as shown. The rods were connected to appropriate power supplies and deposition carried out in a reduced pressure borane system at speeds up to about 8 feet per minute. No arcing occurred, but the filament was wavy as a result of being bent while deposition was going on. This result

made the prospects of using roller and pulley contacts less encouraging unless they were in enclosures which prevent diborane from contacting the filament as it bent around the curved surface.

Of all the designs tried, the freely spinning wheel and leaf spring designs seemed most practical. The latter would require more precise tension and pressure control than was available. None of the contacts tried would appear capable of operating for long periods in a diborane atmosphere because of the probable build-up of contamination on the contact surfaces after a period of time. Thus a manufacturing design with this type of electrical contact would have to provide for either cooling the contacts or shielding them from diborane.

At this point in the program the opportunity arose for investigating indirect methods for heating the filament, specifically by using microwave and radio frequency techniques. These are discussed in the next section.

## C. INDIRECT METHODS OF HEATING

### 1. Introduction

Concurrent with the latter part of the program described above, consideration was given to the application of energy coupling mechanisms which might completely eliminate the need for direct electrical contacts. Of the various possible mechanisms investigated, including IR heating, laser beam, electron beam, microwave and induction heating, the latter two were deemed most promising in terms of both development potential and eventual use in full scale production. They were therefore tried during the third and fourth quarters of the program.

### 2. Microwave Heating

With the assistance of the Barth Electronics Co., a section of cylindrical waveguide was built to accommodate a 24" long, 0.8" diameter quartz reactor tube placed along its axis. This waveguide is shown in Figure 26. The entire laboratory deposition apparatus is shown in Figure 27.

Microwave energy at a frequency of about 2.4 GHz ( $2.4 \times 10^9$  cps) is transmitted by coaxial cables from a commercially available power supply



Figure 26. Close-up View of the Six Cavity Microwave Heater.

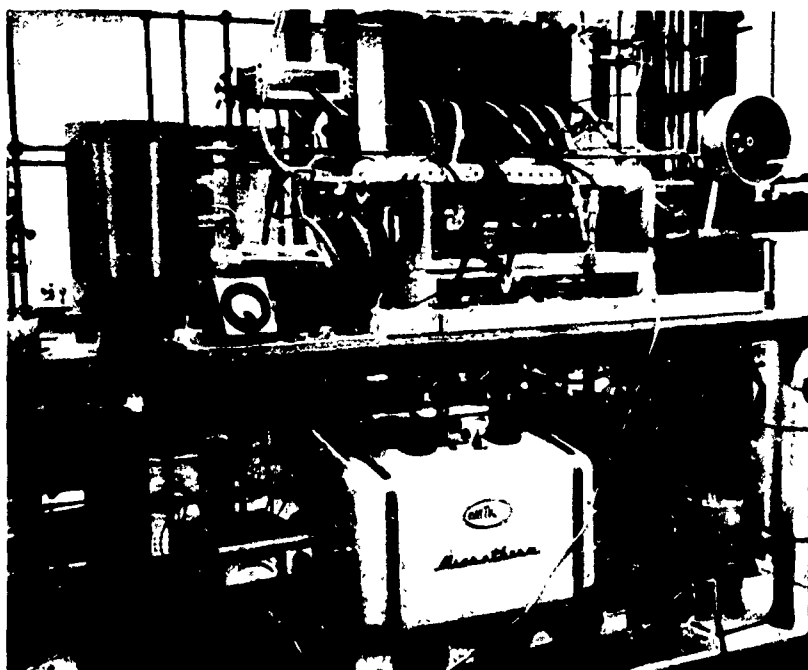


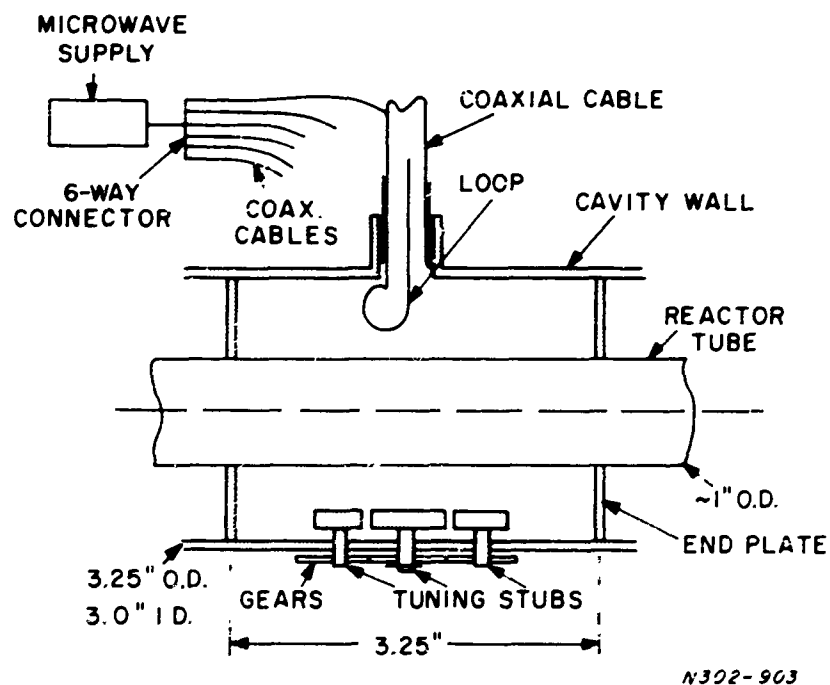
Figure 27. Microwave Heated Boron Filament Deposition Apparatus. Fused Silica Substrates is Fed (from the Vertically Mounted Spool in the Upper Left) Horizontally Through a Fused Silica Tube Inside of the Brass Microwave Cavity Tube and Onto The Take-Up Spool at the Upper Right.

(Raytheon "Microtherm" - 125 Watt) to each of the six sections of the waveguide cylinder.

Each coaxial cable is terminated at the wall of the cylinder by a loop which radiates the high frequency energy into the section. One such section is shown schematically in Figure 28. An end on view of the section in Figure 29 shows the distribution of electric and magnetic fields in the same section. This field configuration is obtained with the plane of the loop oriented along the axis of the cylinder so that the magnetic field lines thread through it rather than run parallel to it. It can be seen in Figure 29 that with this orientation the maximum electric field density is along the axis of the section of the cylinder, where the filament is located.

The end plates of the section of cylinder serve to cause multiple reflections of the electric field waves. Standing waves are thereby set up and each section of the cylinder becomes a resonant cavity in which the field energy is contained (with the exception of that small amount which 'leaks' out through the holes in the end plates establishing a somewhat more complex field pattern).

Another means of altering the amount of energy coupled into the filament (in addition to rotating the loop) is provided by tuning rods as shown in Figure 28. These rods are essentially part of the basic geometry of the cavity and rotating them alters the impedance of this portion of the circuit thereby decreasing the amount of energy available to the filament. Most of the energy not coupled to the filament is reflected by the walls of the cavity back to the power supply. A small amount of energy is absorbed in the walls and causes some heating, which at the power levels in use is negligible. In many cases, in order to minimize this loss and to increase the conductivity of the walls, silver plating is applied. This has been the case with the first stage of heating, where maximum coupling efficiency is desired in order to prevent burnout of the filament once some boron has been deposited on it and its resistance has decreased suddenly from about 250,000 ohms/inch for the cold carbon coating to about 40,000 ohms/in.



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Figure 28. Apparatus for Microwave Heating of Filament (Single Cavity Shown).

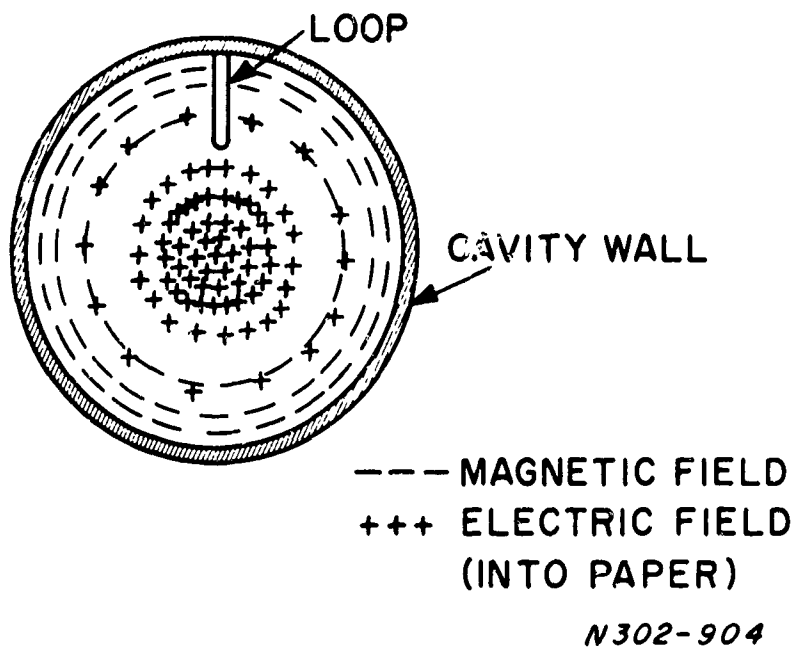


Figure 29. End view of Cavity Showing Field Configurations.

Since each stage requires a different amount of power, it is desirable that the stages should not interact with each other. In the initial apparatus, the stages were not independently variable and any power not absorbed was reflected from the cavity back along its input cable to the six-way connector where it was redistributed and appeared as additional and often excessive power in the other cavities. The installation of a microwave power isolator in the second heating stage prevented interaction of this stage with the other stage during its tuning. However, it was apparent that such isolation was required in every stage.

In spite of the limitations of this first design, several important questions were answered in the laboratory trials. For one thing, it was found that at the desired process pressure of about 20 torr, diborane does not break down and lead to discharge at the power level required to heat the filament. Furthermore, the field established interacts with the conducting filament sufficiently to bring both the carbon-coated silica and boron filaments to deposition temperature. Some lengths of boron filament were produced using this technique. However, the more complete success of the induction heating method and its potentially lower cost in a plant facility obviated the need for further development of the additional equipment which would be required to bring the microwave heating to an equivalent state of development.

### 3. R-F Inductive Heating

The inductive heating technique is based on the fact that a flow of current will be induced in a conductor (e.g. carbon coated glasses) immersed in the magnetic field created by an alternating current flowing through an adjacent conductor (e.g. external field coils). The resistance offered by the conductor to this flow of current results in the desired heating of the conductor ( $I^2R$  heating). Since non-conductors will be unaffected by the magnetic field, the glass reactor walls surrounding a conducting, carbon-coated glass filament will remain cool, with the exception of heat radiated from the hot filament itself. Any gaseous components flowing through the reactor will,

likewise, be heated primarily through direct contact with the hot filament, thus permitting the diborane pyrolysis reaction to occur at the filament and in no other place. In addition to other advantages which are discussed below, the most obvious advantages of this technique are, therefore, the absence of contacts, either liquid or solid, and the ability to easily control the location and magnitude of heating.

In actual practice, the power source used is an induction heater (Sherman, Model SD-42) rated at 4KW output at a frequency of 24 MHz ( $2.4 \times 10^7$  cps). In initial runs, the transmission line from the output coil of the power supply to the exterior of the reactor tube consisted of two 15-foot lengths of 1/8" diameter copper tubing, each wound at intervals around a Lucite tube to form three single turn coils of about 3" diameter. The coils were placed on the tube to form five pairs and to provide a potential for five zones of heating of the filament as it was drawn through the glass reactor enclosed by the Lucite tube (see Figure 30). In use, this line with the coils equally spaced provided three visible areas of heating, with the two other zones at a somewhat lower temperature. The relative amount of heating and the number of stages heated to luminosity was varied by altering the coil spacing.

The second transmission line tested consisted of two 4-foot lengths of copper tubing, each terminating in a single turn coil and each having in parallel with it two additional single turn coils. The coils of one line were also placed alternately with those of the other to constitute five pairs (see Figure 31). In initial tests with this line, five zones of heating were observed along an approximately 3-foot length of filament. In later tests, zones of heating over a length of 4 feet were obtained by adding five more coils. The power output required for heating the above length of filament, which had a room temperature resistance of 260,000 ohms per inch, was about 200 watts. Substrates with resistances ranging from  $2 \times 10^4$  ohms/inch to as high as  $5 \times 10^6$  ohms/inch have been successfully heated to deposition temperatures and coated to produce 4 mil diameter boron filament in a continuous manner at speeds up to 13 ft/minute.

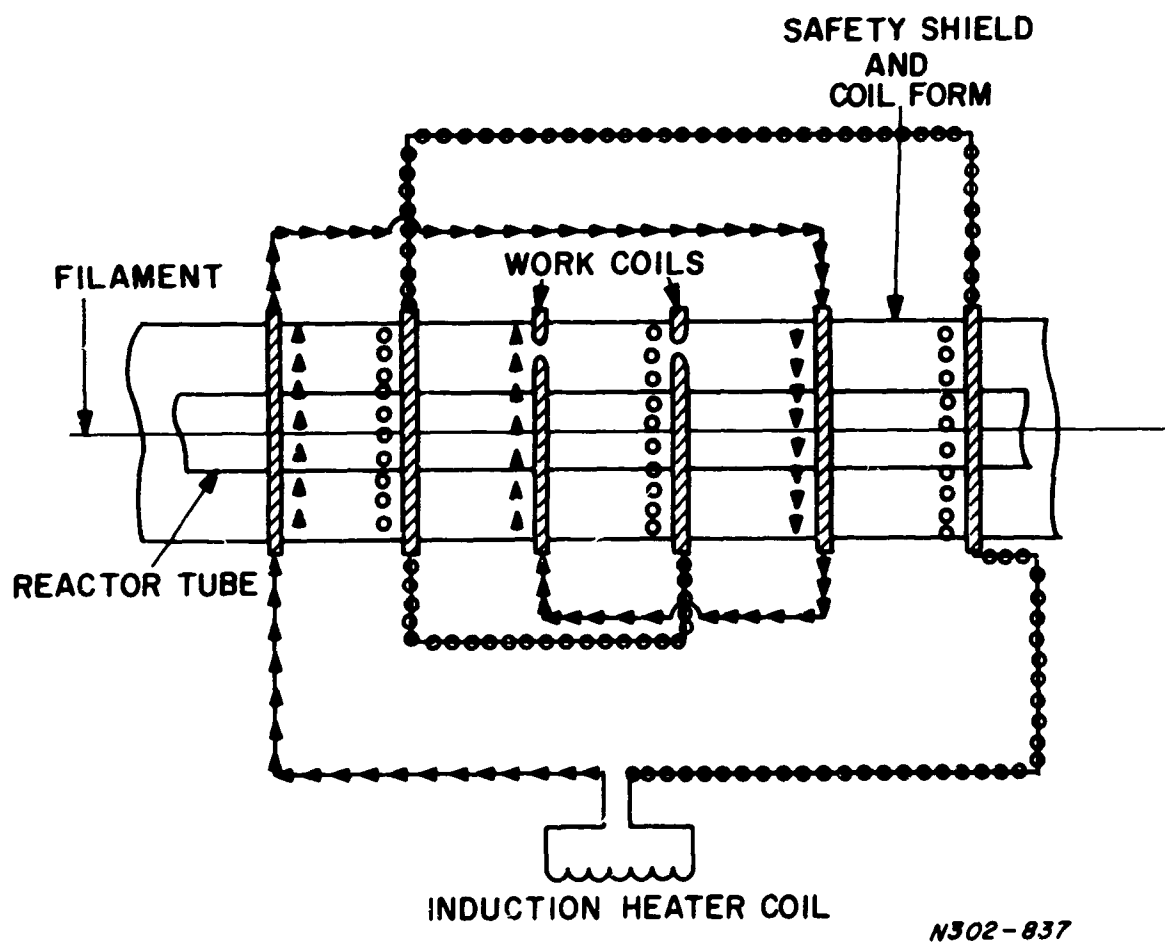


Figure 30. Initial Transmission Line Configuration for Inductive Heating.



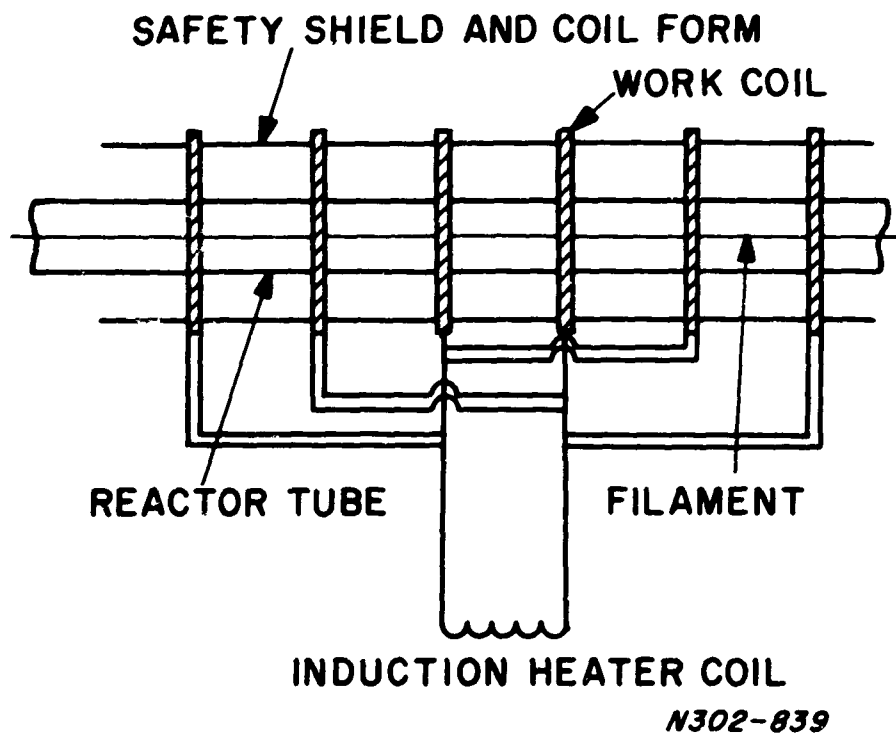


Figure 31. Improved Transmission Line Configuration.

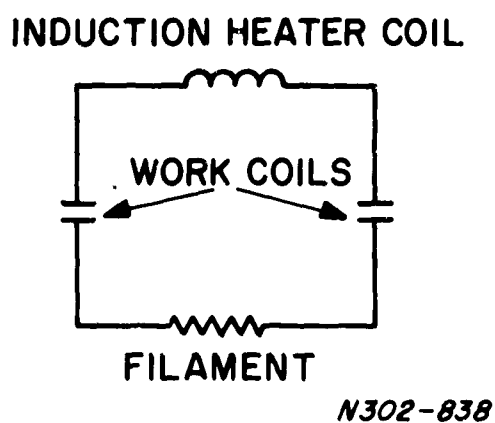


Figure 32. Equivalent Circuit.

Although the basics of the mode of energy coupling have been mentioned above, it may be instructive to consider any one heating stage as a circuit in itself, analagous to a simple LRC circuit shown in Figure 32. The filament is not only a series resistance which absorbs most of the energy of the circuit, but is also an element of each of two coaxial capacitors whose energy is determined by the ratio of coil diameter to filament diameter, and by the length of coil (which in this case is the thickness of the coil). The heating of the filament can therefore be varied by changing the coil diameter and thickness and by changing the series resistance, i. e. the distance between coils. This provides a means not only of regulating the overall temperature of the filament, in addition to that provided in the power supply, but permits convenient changes in the temperature gradient along the length of the filament. In practice, changes in coil spacing with the fixed coil diameter have been found to be most convenient in adjusting the filament temperature gradient. Another development of these initial runs was the ability to heat four boron-coated filaments simultaneously in a single tube, along a length of about three feet, to what appeared to be a uniform temperature. This capability shows promises of greatly simplifying large scale production procedures through the use of multifilament reactors.

The nine stage transmission line and power supply described above have been used with the cross feed reactor shown in Figure 33, to produce boron filament from diborane pyrolysis on pyrolytic carbon coated silica and Vycor substrate and on "Aquadag" carbon-coated "177" glass. The external features of this reactor were similar in design to those of the mercury pool contact reactor described under Task IV. The interior gas distribution baffle was also similar with the important exception that it was fabricated entirely from epoxy-fiberglass and Textolite and contained no electrodes or filament guides other than were provided by the differentially pumped end caps.

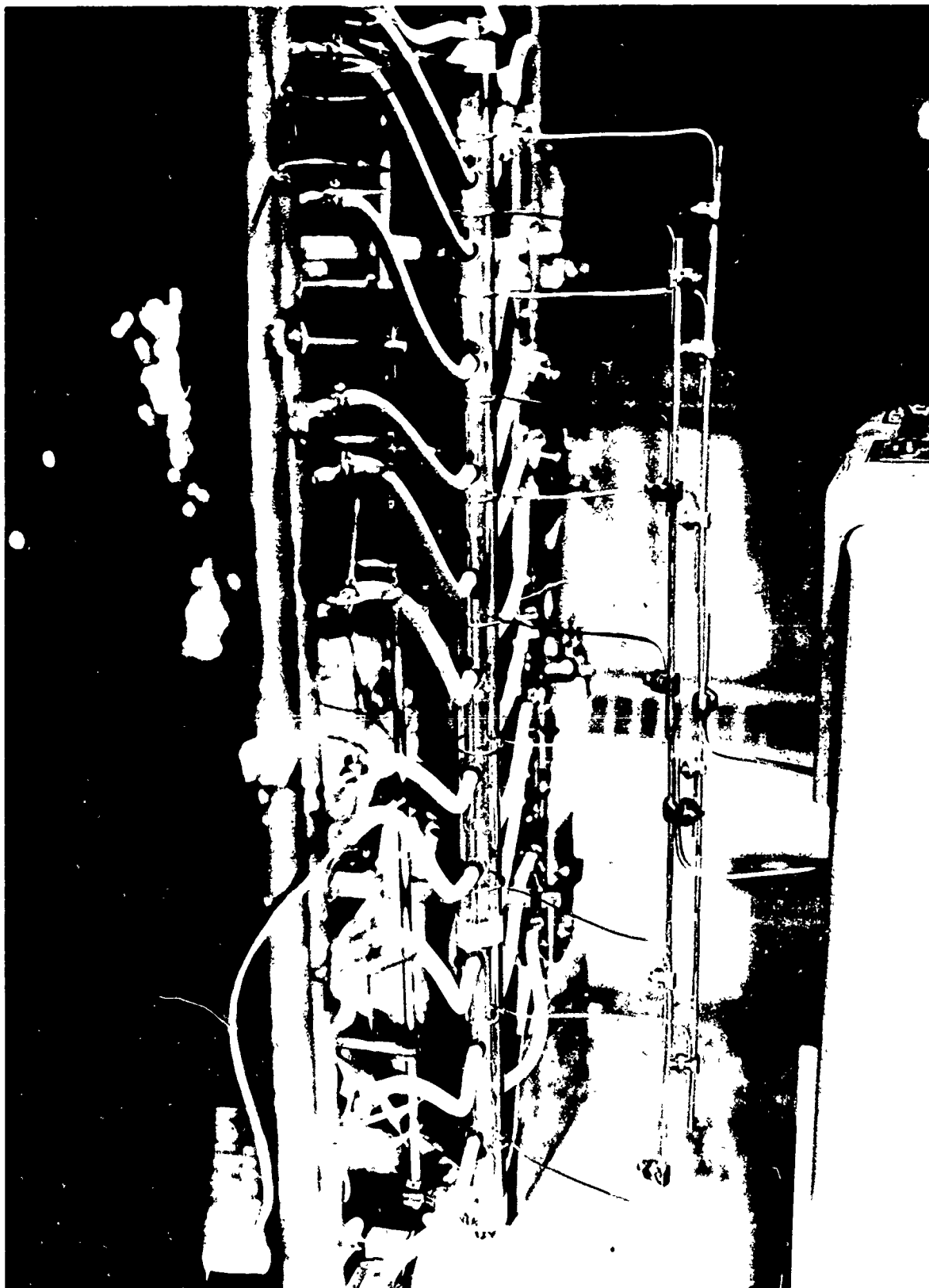


Figure 33. RF Heated Prototype Cross-Feed Reactor.

The various carbon coatings applied to the bare substrates used accounted for the greater than two order-of-magnitude range of resistances mentioned above. Nevertheless, deposition of boron to a desired diameter could generally be accomplished for all of these materials at the same filament speed, gas feed rate, reactor pressure, gas baffle geometry, and power level, by changing the length of the first stage or the diameter of the first stage work coil, while holding the other stage lengths fixed. This might be expected in view of the fact that the conducting substrate is primarily heated boron rather than carbon after passage of the filament from the first stage.

Except for the electrical parameters involved in the RF coupling technique, the conditions of operation used in the mercury pool reactor described below were essentially duplicated in the RF prototype reactor and virtually no effort was devoted to altering the basic process parameters established previously. Although the data and detailed results will be presented in Task IV, it is significant to note here that runs were made in which the average tensile strength of boron on silica was as high as 380,000 psi with average values in excess of 300,000 psi typical for a prototype reactor in which a total of more than 6000 ft. of  $4 \pm .1$  mil diameter filament was produced.

On the basis of its ease of use, the quality of the product produced, the elimination of electrical contacts, and other factors to be elaborated upon below, the RF heating technique appears to be particularly well suited for development as the nucleus for a high speed production facility.

## SECTION V

### TASK IV A - PRODUCT AND PROCESS IMPROVEMENT

**Objective:** To improve deposition rate and mechanical properties of filaments made by decomposition of diborane on glass and to obtain basic chemical and material balance information to facilitate economic analysis of a high production rate manufacturing process.

#### A. BACKGROUND

Several essential characteristics are necessary in a successful, economical manufacturing process. These are, among others, a high production rate, a uniform and acceptable product, and economical use of raw materials. In the case of boron filaments on glass (silica), an earlier program demonstrated that it is possible to make strong material, i. e. with average tensile strengths well over 400,000 psi, but the reproducibility was poor. Hence, it was necessary to accumulate sufficient operating experience and background information to pinpoint sources of weak filament as well as to develop conditions of maximum efficiency regarding the conversion of diborane to filament. The complex chemistry of diborane at lower temperatures, where polymerization reactions occur which reduce the amount of diborane that can be recycled, necessitated a study of the chemical reactions occurring in the reactor and a determination of as realistic a material balance as possible, under various operating conditions. Several side studies were undertaken to support the main line of investigation. These consisted of efforts to increase deposition rates by rendering the substrate capable of withstanding greater temperatures in the initial part of the reactor and an analysis of filament failure with respect to reactor conditions, i. e., geometry, method of heating, electrode configuration, process conditions and their effects on filament morphology. The accumulation of this information using a prototype of the current mercury contact reactors constituted an essential step in the scale-up of a process from pilot plant level to manufacturing level, since it is in this step that major variations can be expected in reactor configuration and gas handling conditions. As was expected in a reaction sequence

of this complexity, process and product improvement do not necessarily go together, and operating conditions representing a reasonable trade-off must result from a study of the interaction of process, economics, and filament properties.

In the program, separate lines of investigation were pursued in the areas of deposition rate increase, filament properties, material balance and analysis, and reactor design and conditions, which converged toward the end of the program into a single reaction system, producing acceptable and reproducible filament at what is believed to be maximum efficiency within the limits of the reactor enclosures studied. Additional improvements in efficiency can be achieved by following the direction in design of reactors pointed out by the results of these studies. Although efforts to increase deposition rate beyond the levels presently achievable resulted generally in the production of weaker filament, these efforts were overshadowed by the difficulty of obtaining a true response from the filament as to the effect of process variation. As the program developed the causes for high scatter became visible and were largely eliminated. However, it was not possible then to reopen the process study with respect to increasing deposition rate in the absence of high scatter. Consequently, the high deposition rate conditions for the successful operation of a high speed reactor remain to be determined.

The deposition rate studies were primarily carried out using pyrolytic carbon-coated silica substrate in parallel with the development of a carbon-coated glass substrate as previously described in Tasks I and II. As experimental quantities of other coated glasses became available, they were examined in the best practical way, i. e., by deposition of boron under normal operating conditions.

All considerations concerning reactor design and the effect of operating conditions on filament strength were made with an integrated high speed reactor in mind as the ultimate goal of the studies reported below. Every effort was made to evaluate both conditions and geometry within this

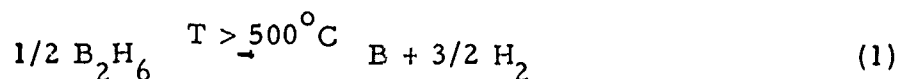
framework in order to settle as many questions as possible regarding the interaction between design and product properties prior to entering Phase II of the program in which the physical design and construction were to have been undertaken. A summary of these conditions is presented at the end of this task in the light of the knowledge gained in the preliminary results reported next.

## B. DIBORANE PYROLYSIS AND POLYMERIZATION

Because of the close relation between reactor design, filament properties and material balance, a brief description of the chemical processes involved in the formation of boron filament, and its by-products, is warranted at this point.

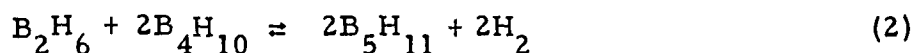
Decomposition of diborane and hydrogen at micron level pressures, and at a heated substrate always involves the formulation of intermediate boron hydrides as well, because of the temperature gradient extending from the hot surface to the reactor wall. Knowledge of the qualitative and quantitative aspects of intermediate hydride formation is of vital necessity in optimizing both filament properties and process economics. Until recently, the technical and economical effects of by-products of the diborane pyrolysis were studied only as a subordinate aspect of the effort to achieve good filament properties. However, analytical instrumentation made possible the acquisition of more precise information about the interplay between diborane decomposition and polymerization reactions and the effects on filament properties and process efficiency.

Although a complete survey of borane chemistry as it pertains to filament formation will not be attempted here, several features will be discussed which are of primary importance in this connection. For the purpose of the discussion, two reaction sequences originating with diborane can be considered. The first, decomposition, is expressed by the equation:



The second sequence is more complex, occurs above 0°C, and involves the condensation polymerization of diborane to higher molecular weight species. Various mechanisms have been proposed<sup>(7)</sup> which require a number of intermediate species stable only long enough to continue the reaction sequence. These are of no immediate concern. There are also several relatively stable so-called intermediates which are isolable and which persist throughout the reaction system. These are tetraborane-10 (B<sub>4</sub>H<sub>10</sub>), pentaborane-9 (B<sub>5</sub>H<sub>9</sub>), decaborane (B<sub>10</sub>H<sub>14</sub>) and less well characterized structures known collectively as "borane polymer" or yellow solids". The first three are vapors under reactor conditions and are found in the reactor and exhaust gases, together with diborane and hydrogen in relative proportions which depend on the reaction conditions chosen. Under certain conditions they appear in the feed gas in minor amounts. The remainder, decaborane and heavier molecules, are solids which condense in the process lines. As such they may continue to react more or less rapidly with diborane gas passing by, depending on the local temperature.

Since a thermal gradient exists in the reactor between the filament surface and the reactor wall, the polymerization reactions will occur to an extent determined by the gradient, composition, pressure and residence time of the gas in the reactor. The details of the reactions which produce the intermediates are somewhat varied with each reaction environment. About the only well known equilibrium is that involving tetraborane-10 and pentaborane-11:



which establishes itself in the gas phase at all temperatures at which the components can be present as gases. Adler and Stewart (8) determined the kinetic constants for both the forward and reverse reactions, as well as the equilibrium constant at several temperatures in the vicinity of 100°C. The rate of change of these values with temperature in the small range studied by these authors indicates that the approach to equilibrium should be extremely rapid at temperatures near that of the filament surface,



i.e., temperatures which probably prevail in the boundary layer around the heated filament. Thus, the electrodes and reactor walls typical of most of the equipment used thus far (see below) would provide sites at which formation of pentaborane-11 and tetraborane could occur at various rates. Assuming that these species are useful in making filament, and not harmful to properties nor wasteful of diborane, their presence can be tolerated to some extent. Until this extent is known, and in the present cryogenic trapping system, their presence is wasteful since they cannot be recycled efficiently as part of the feed gas mixture. Their effect on filament properties also could not be precisely determined. Data will be presented on these points in a later section. At this point it is sufficient to state that the species of interest in the borane polymerization cycle are the members of the equilibrium discussed, as well as the relatively stable and isolable pentaborane-9 and decaborane. Yellow solids of course, are extremely important since they can be neither recycled nor recovered as by-products as can pentaborane-9 and decaborane.

In summary, the elements of reaction procedure and reactor design of importance in producing acceptable filament efficiently are those associated with gas residence time, temperature at the filament and of various reactor components, gas flow pattern and gas feed composition.

### C. REACTOR DEVELOPMENT

#### 1. Mercury Electrode Reactors

As has been pointed out, the preparation of boron filaments by the thermal decomposition of diborane is greatly dependent upon the total reaction environment. Therefore, at this point it is helpful to describe the equipment which has been used before proceeding to its probable effects on borane polymerization reactions.

In order to decompose diborane in preference to polymerizing it, it is necessary to provide (a) a heated substrate, (b) efficient delivery of the feed gas to substrate, and (c) minimum probability for polymerization reactions to occur. These conditions have been at least partially achieved

in the laboratory pyrolysis reactors described elsewhere in detail <sup>(9)</sup>. In essence, they consisted of tubular chambers along the axes of which the filament passed. A low pressure in the reactor was achieved by using differentially pumped endplugs provided with nitrogen purge chambers. The gas was delivered at right angles to the filament through a collimating slot which provided a uniform velocity for the gas along the length of the filament. The filament was heated by means of a high-voltage, low-amperage, alternating current obtained from neon light transformers connected to the secondary of a variable transformer. Contact was made with the filament by means of mercury-containing electrodes, either as vertical standpipes in a horizontal reactor, or as horizontal cups in a vertical reactor.

Figures 34 and 35 illustrate these reactor concepts, the former of which has been termed a laboratory reactor and the latter a prototype pilot plant reactor. In the latter case, the reactor dimensions have been limited to two diameters, 3/4" and 1-1/2" by 46" long, while the laboratory reactors have always been 3/4" diameter, but of varying length. These details of construction have an important bearing on the course of the reactions occurring within them because of the sensitivity of the feed gas to excessive temperature for long periods. Consequently, the wall temperature, mercury and mercury electrode temperature and gas flow characteristics are factors which must be understood in their relationship to gas chemistry, filament properties and material balance.

## 2. Radio Frequency Heated Reaction System

This is discussed in greater detail in Task III. However, the preparation of filament in Task IV, used a reactor configuration identical to the mercury electrode system with the exception, of course, of the contacts required in the latter.

Optimization studies were carried out in the laboratory reactor as well as in a prototype of the pre-pilot plant reactor, with respect to diborane pressure, feed rate, temperature, filament draw speed, and power settings (temperature). The result was a set of so-called standard conditions which



Figure 34. A Six Stage 28" Laboratory Reactor Including the Filament Feed and Takeup Reels, High Voltage Transformer Power Supplies for Each of the Stages and the Flow Meters for Diborane are shown.

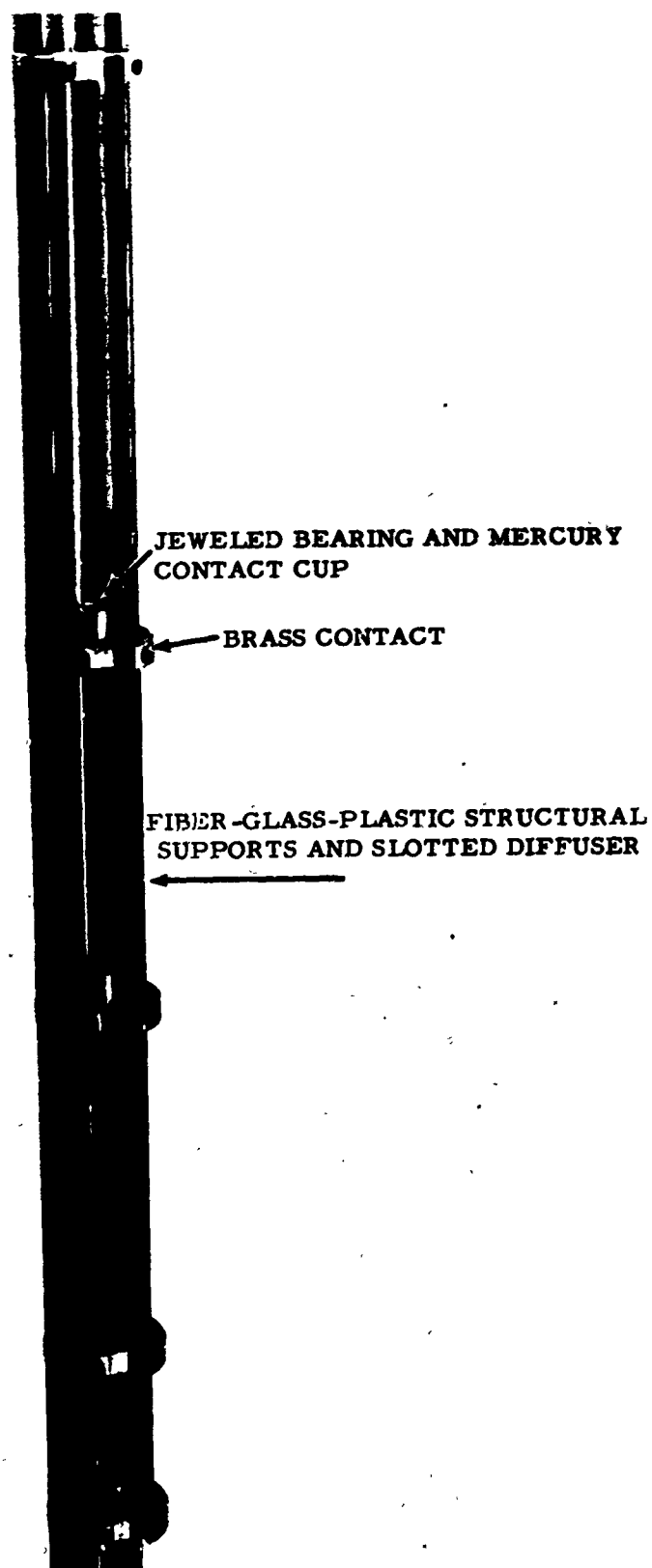


Figure 35. Reactor Insert Closeup to Show the First 4 Stages of a 9-Stage Prototype Unit, Showing Design of Open Cup Mercury Electrodes.

most often yielded 4.0 mil filament having an average tensile strength above 300,000 psi. These standard conditions were:

- (a) Filament Speed, 12-15 feet per minute
- (b) Reactor Pressure, 19-22 torr
- (c) Feed Rate, 30-40 cc/min./inch of hot filament
- (d) Power settings varied more due to the multiplicity of stages and need not be listed there. However, since no method was available for monitoring or controlling filament temperature, variations were made by altering the power settings.

In operation, gas feed conditions were established after pumping out the reactor, operating pressure achieved, and the power was applied to the filament. Power could be turned on by a switch -- no slow approach to full power (temperature) was required.

#### D. DEPOSITION RATE IMPROVEMENT

Inasmuch as the economics of filament production on a large scale are determined largely by labor cost per pound of filament, it was important to investigate the possibility of increasing the production rate intrinsically, i.e., by altering the process rather than simply multiplying the number of units employed to make the filament. While deposition rate could be improved to some extent for example by more precise alignment of the filament with the collimating slot in the reactor, a major increase in rate should be achievable by an increase in deposition temperature. The deposition of boron from diborane is a kinetically controlled process, i.e., the boron deposition rate is limited by the rate at which deposition species are formed at the surface, rather than by the rate of material transfer through the gas phase to the surface<sup>(10)</sup>. From an extension of the rate curve in Ref. 10, a rate of about 2400 mils per hour or roughly twice the present rate could be achieved in the vicinity of 800°C, provided of course the filament was acceptable. It was on this basis that the preliminary high speed reactor design length of 100-110 feet of heated filament was chosen for filament speeds near 1000 ft./min. In addition to increasing the temperature of the major portion of the deposition, it was believed that an

increase in the deposition temperature of the initial stages of the multistage reactor could be achieved by altering the surface of the substrate so that temperatures would not be limited to the vicinity of around  $600^{\circ}\text{C}$  (average). The limitation is required by the formation of a very bright spot ( $700\text{--}750^{\circ}\text{C}$ ) at the location where the carbon-coated filament first encounters diborane. Efforts to increase the average temperature of the first stage and often the second as well, cause the so-called hot-spot to become still hotter and to break the filament. This phenomenon has been observed only when the carbon surface is exposed. Experiments in which a thin tungsten coating was applied prior to deposition of boron from diborane were carried out with a 50% increase in draw speed and no loss in diameter as a result of being able to operate the first stage at a higher temperature. At the same time, it was observed that it was possible to achieve temperatures close to those required to deposit boron on a carbon coated filament in the  $\text{BCl}_3\text{--H}_2$  system, and that, with care, boron could be deposited at a low rate in a single stage system at low filament speeds.

A double laboratory reactor system, shown in Figure 36 was built for the purpose of integrating these two deposition processes in series. The halide reactor was mounted horizontally while the low pressure hydride reactor was vertical and at right angles to it. Initially both were cross feed gas flow systems but early results in halide deposition with this arrangement yielded extremely weak and somewhat crystalline filament (Figure 37). Under these circumstances, the filament would not negotiate the right-angle turn into the hydride reactor. After changing to a parallel feed system, the halide process in single system operation produced diameter increases of about 0.1-0.5 mil in four stages, with the last stage operating at about  $1000^{\circ}\text{C}$  (Figure 38). Stoichiometric gas mixtures of boron trichloride and hydrogen were used throughout.

Initial studies of hydride deposition at temperatures very much in excess of those established in earlier optimization studies produced filament at higher rates, but of somewhat inferior properties. At the maximum rate

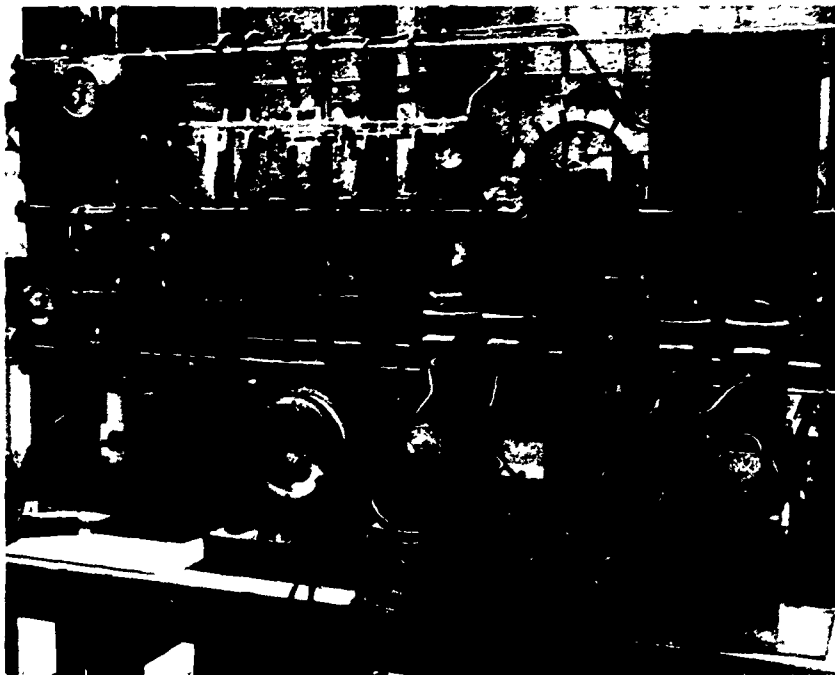


Figure 36. Tandem Horizontal  $\text{BCl}_3\text{-H}_2$  Reactor and Vertical (left side of picture)  $\text{B}_2\text{H}_6$  Low Pressure<sup>2</sup> Reactor for Applying a Precoat of Boron from  $\text{BCl}_3$  and the Principal Boron Coating from Diborane.



Figure 37. Precoated Boron on Silica Filament Made in the Cross Flow  $\text{BCl}_3$  Reactor, Showing Crystalline Nature of the Coating (420X)

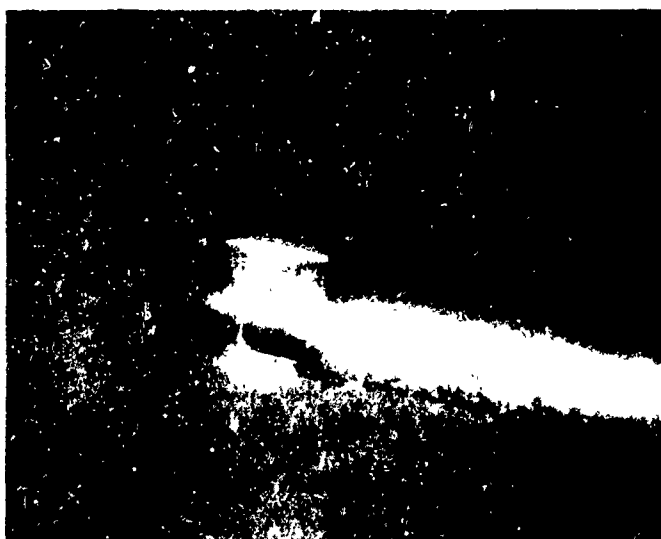


Figure 38. Precoated Boron on Silica Filament Made in the Parallel Flow  $\text{BCl}_3\text{-H}_2$  Reactor Showing a Smoother, Less Crystalline Surface (593X)



achieved, approximately 1000 mils per hour, a maximum average tensile strength of 290,000 psi was obtained. To prevent excessive production of borane polymer at these higher temperatures, reactor pressure was reduced, which in turn decreased the deposition. Table XI shows typical results in a series of experiments conducted in an effort to balance these factors - minimum polymer formation, maximum rate and acceptable strength. In further experiments along these lines, i. e., at increased temperatures using the prototype reactors, both 3/4" O.D. and 1-1/2" O.D., extremely weak filament was made while excessive polymer formation occurred. In the light of failure to achieve a satisfactory filament in this apparatus at the higher rate, further experimentation was delayed until a better understanding of the reactor chemistry could be gained and development of material balance techniques completed.

It is important to note, however, that in these experiments, as well as in those to be discussed in connection with property improvement effort, mercury electrodes were used. As the program developed, it became evident that these were the source of random contamination through excessive pyrolysis which affected filament strength so as to obscure the result of variations which were purposely introduced into the experiments. Inasmuch as the RF heated reactor does not have these reactive surfaces, it cannot be said that the present operating conditions are the best with respect to the tradeoff between rate and properties. Two major areas remain to be explored in the RF heated reactor: process conditions and reactor geometry.

#### E. PRODUCT IMPROVEMENT

A considerable portion of the boron filament prepared in the prototype and pilot plant reactors was characterized by rather wide variations in tensile strength. Values from close to 500,000 psi to less than 20,000 psi were sometimes found within a few inches of each other on material made under apparently identical conditions, i. e., within a few seconds. Efforts to optimize filament tensile properties through programmed adjustments of reaction parameters were therefore hampered by the difficulty of distinguishing a significant variation from a process change from that due merely to

TABLE XI

RESULTS OF RUNS TO IMPROVE DEPOSITION RATE OF BORON ON CARBON COATED SILICA

Run #	Reactor Pressure (mm)	Reactor Speed (ft/min.)	Reactor Length (in.)	Filament Diameter (mils)	Growth Deposition Rate (mil/hr.)	Average Tensile Strength (ksi)
70-2	21	13	46	4.2	650	174
71-3	24	18	46	4.7	1020	161
71-5	24	22	46	4.05	1030	160
72-2	23.5	19	46	4.4	1000	290
73-2	23	15	46	4.2	760	230
75-1	22	16	46	4.0	750	250
25-1	13	4	20	5.1	600	103
25-2	15	4	20	5.5	720	143
25-3	16	6	20	4.6	865	107

to the scatter in strength values. Conversely, material produced under ostensibly identical conditions often yielded quite different average test results, regardless of scatter. Figure 39 illustrates this point. It shows the breaking stress of samples from two identical runs versus the nearest neighbor population, i.e., the number of specimens having values above and below a particular center value, as expressed by

$$n'_o = \frac{n_{-1} + n_o + n_{+1}}{3}$$

In both cases, the filament diameter was 3.3 mils. Run 18-5 had an average tensile strength of 330,000 psi while Run 19-1 averaged 260,000 psi. The statistical representation of these data indicates why the averages are different, but it does not reveal the causes of the individual differences. However, microscopic examination of both materials, in toto as well as of individual fracture surfaces, showed the following:

- (a) Filament failure was always associated with an isolated nodule, tangent to the plane of failure (Figure 40)
- (b) Filaments having a lower average strength appeared to have considerably more nodules per unit length than the stronger material (Figure 41)
- (c) Larger nodules were associated with lower strength failures
- (d) Examination of a large number of nodules and filament failures disclosed what appeared to be two different types - those which were extremely large and irregular (Figure 42) and those which were relatively symmetrical and which varied in both diameter and height above the filament surface. Both could be severe stress raisers, whereas another characteristic, nodule type appeared to be less severe. It was usually broader and lower than the nodules associated with low stress failures (Figure 43) and could be found on an intact portion of the filament within the gage portion of a low strength failure.

While the nodules could be associated with individual low strength failures and a large scatter in values, there was also evidence that preparation of filament under conditions considerably different from so-called optimum conditions could lead to a material which was uniformly weak and subtly different in surface appearance from strong sections of filament made under optimum conditions. Table XII illustrates this point. Conversely,

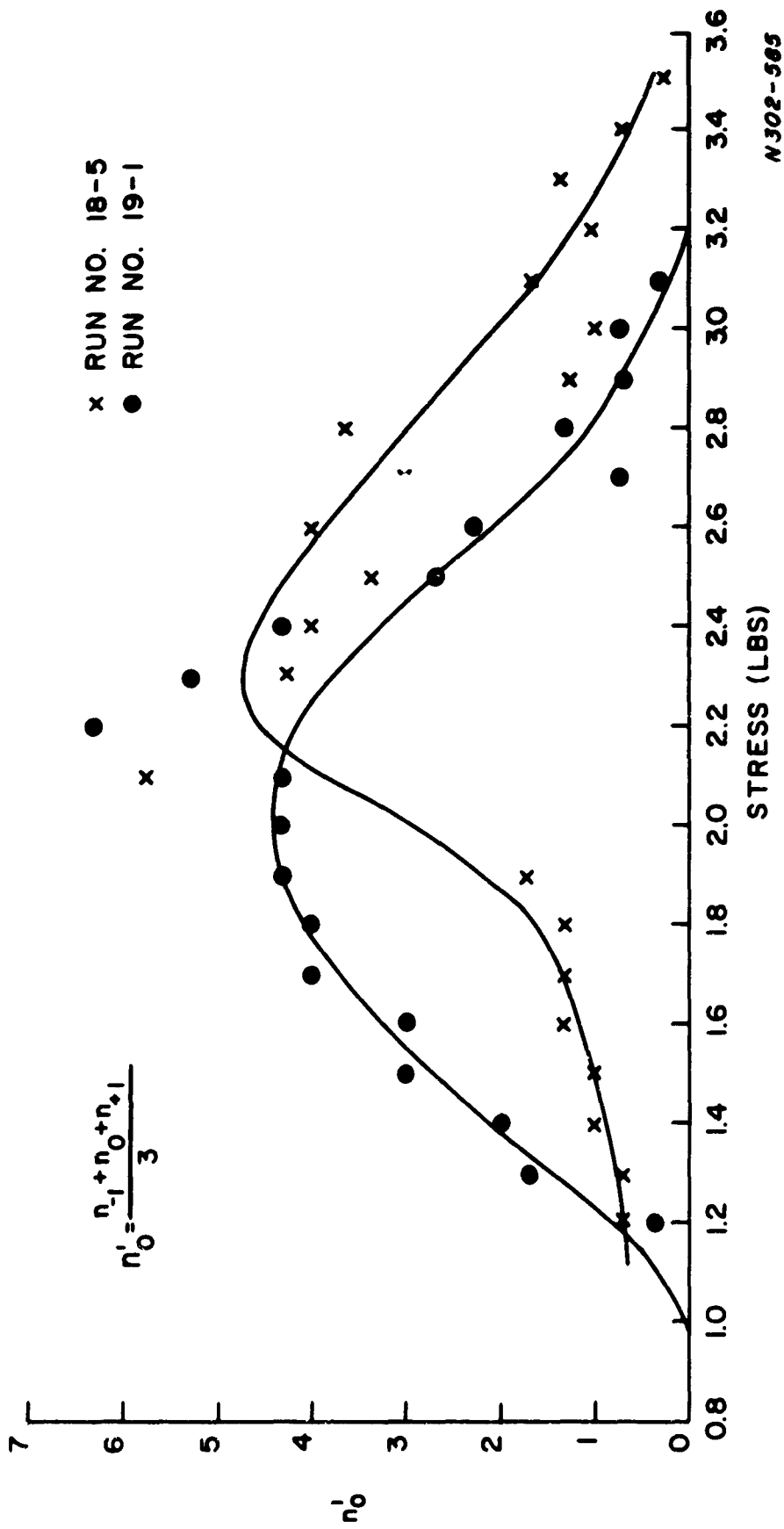


Figure 39. Breaking Stress of Samples from Two Runs of Boron on Silica Versus Nearest Neighbor Population of Sample.



Figure 40. Typical Appearance of Low Stress Failure Showing Nodule Tangent to Failure Plane (593X), Nodule Height  $2 \times 10^{-4}$  in Nodule Diameter  $6 \times 10^{-4}$  in.

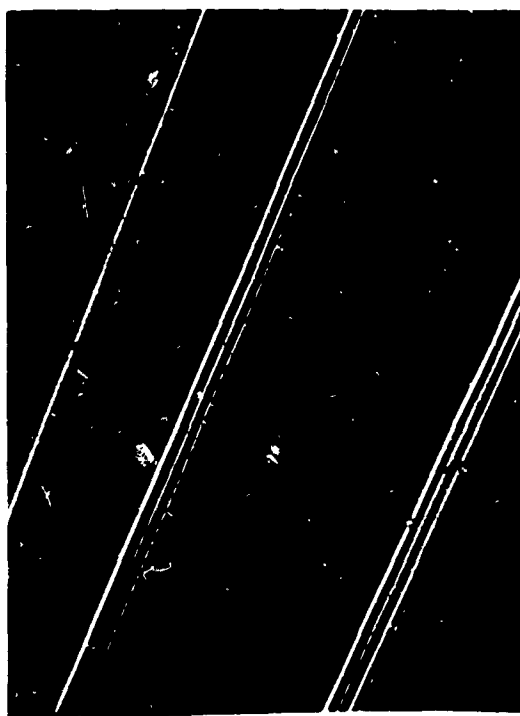


Figure 41. Appearance of Low Average (Left) and High Average (Right) Boron Filament (40X).

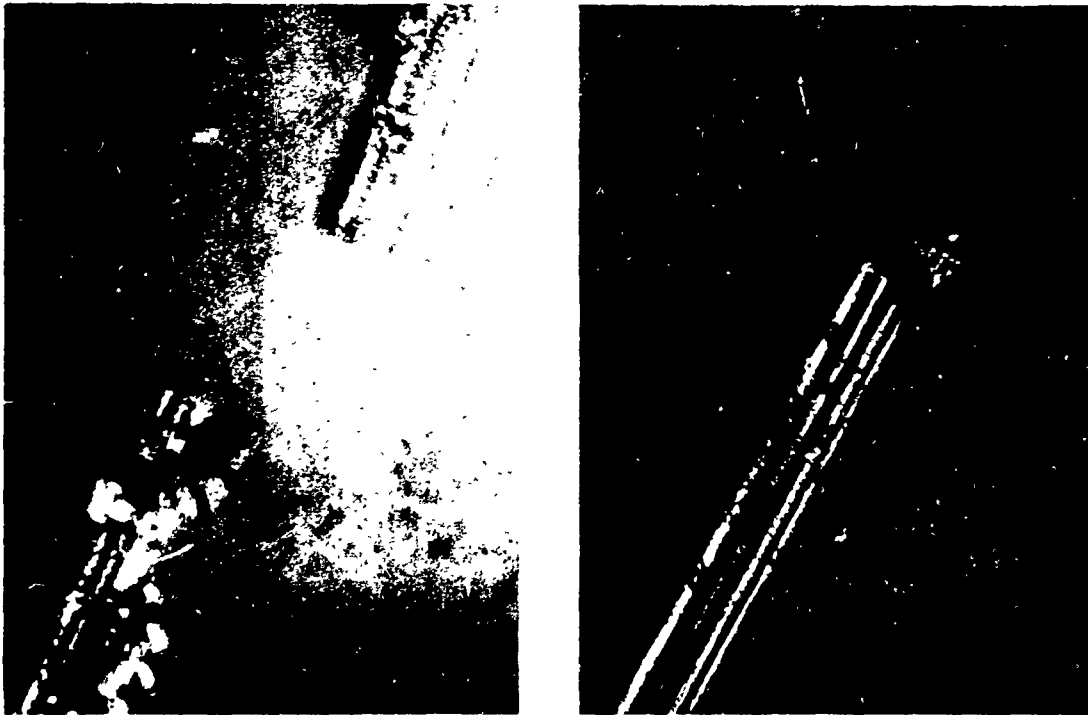


Figure 42. Large Irregular Nodules Due to Massive Inclusions (116X).

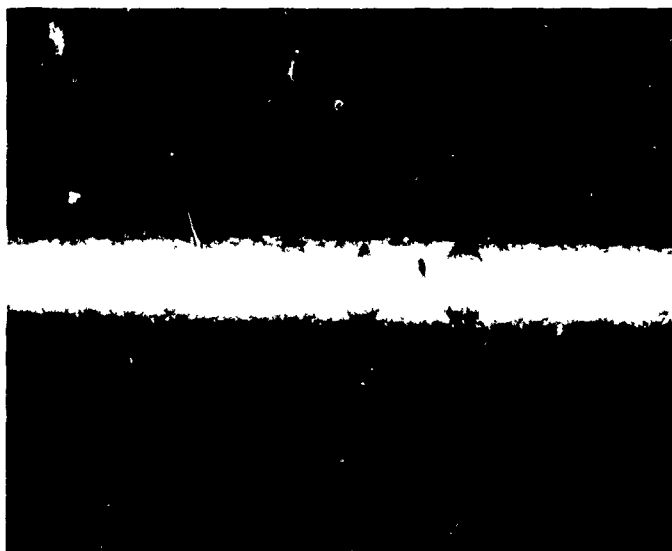


Figure 43. Broad Low Nodule in Gage Section of Filament Prepared in RF Heated Unit (490X). Tensile Strength at Adjacent Failure = 456,000 psi.

**TABLE XII**  
**EFFECT OF INCREASED TEMPERATURE ON**  
**DEPOSITION RATE AND TENSILE STRENGTH**

Run 2-19 Optimum Process Conditions					Run 2-16 Higher Deposition Temperature (10% Power Increase)				
Time After Start (min.)	Tensile Strength (Ksi)			Diam. (mils)	Time After Start (min.)	Tensile Strength (Ksi)			Diam. (mils)
	High	Low	Avg.			High	Low	Avg.	
0	340	192	273	4.0	0	227	131	193	4.3
10	340	266	295	4.0	10	273	140	221	4.2
20	329	170	240	4.0	20	262	131	192	4.3
30	266	159	240	4.0	30	287	191	243	4.2
40	251	133	199	4.0					
50	259	138	215	4.0					
60	358	188	273	4.0					
70	356	257	306	4.0					
80	348	204	275	4.0					
90	377	162	304	4.0					
100	397	188	311	4.0					
110	386	238	310	4.0					
120	431	166	282	4.0					
130	363	136	267	4.0					

filament which was characterized by a high average tensile strength had fewer low breaks. Although the scatter might still be wide, it covered a higher general strength range.

The importance of nodules as a primary cause for low stress failures can be brought out by these considerations. Boron deposited on silica from diborane is a brittle glassy material which, as a result of thermal expansion coefficient mismatching, is under slight residual tension (20-40,000 psi) at the outer surface. All observed failures with a few recent exceptions have initiated at the outer surface rather than at the core/deposit interface as is the case with boron/tungsten filaments. No interaction occurs between the deposit and the core (excluding any reaction with the very thin non-load bearing carbon conductive coating), and the deposit/core system is mechanically similar to a shrink fit. The nature of this material would make it particularly sensitive to the presence of an isolated stress

raiser, such as a nodule. The difference in diameter of the filament at the center of the nodule and at its edge, the sharpness of its radius of curvature, and the depth or sharpness of the discontinuity where the nodule rises from the filament are contributing factors in this picture<sup>(11)</sup>. If, on the average, a nodule represented a stress concentration factor of about 1.5, a relatively mild notch, the strength of the filament at that point could be reduced from 350,000 psi, for example to about 230,000 psi. The frequency of appearance of nodules along the surface is another important factor. A profusion of rather small nodules could give rise to a relatively uniform material of intermediate strength; fewer but larger nodules could give rise to material which had a few very high strength breaks, but a sufficient number of low strength failures to bring the average down, and indeed to make the filament unhandleable with respect to its future use, i. e., in making tape.

With these indications of the role played by surface imperfections in the scatter of tensile strength values, the deposition process was analyzed for causes or origins for such nodules. The following listing was arrived at and each possibility checked out experimentally in order to eliminate it as a significant factor or to remedy it if possible.

#### POTENTIAL CAUSES FOR NODULES

1. Substrate defects (soot, nodules, holes).
2. Substrate dirt, absorbed from the atmosphere.
3. Absorbed moisture on the substrate, particularly in sooty regions.
4. Arcing and discharging at mercury electrodes.
5. Dust blown into reactor with feed gas.
6. Dust on reactor walls from reaction by-products.
7. Deposition of high molecular weight borane fragments, and increased local deposition rate.
8. Sooting in the region around the filament, and deposition of solid high molecular weight fragments.
9. Dirt pickup at electrodes.
10. Mercury pickup at electrodes.

The discussion of results of the experimental program mounted to identify and eliminate nodule causing situations may be conveniently divided into work associated with the substrate, the electrical power system, and the deposition process itself.



## 1. Substrate Effects

A series of experiments was carried out to evaluate adherent defects on the substrate as the cause of formation of severe nodules. Three primary sources were suspected: adherence of soot, generated during the pyrolytic coating process, adherence of accidentally contacted dust or lint from the laboratory atmosphere during storage and running, and adsorption of moisture on either the filament itself or on adherent dirt or soot. Examination of random pieces of the carbon coated silica showed that the entire length was not always glassy smooth. Adherent particles such as those shown in Figure 44 were fairly common among the pieces examined, but how frequently they occurred in a length of several thousand feet cannot be estimated. Efforts to bring about an improvement in filament tensile strength, assuming such substrate defects were responsible for scatter and low values, consisted of (a) using a radioactive brush to discharge the static charges on the filament and brush off dust and lint prior to entrance of the filament into the reactor, (b) precleaning the substrate ultrasonically in alcohol, (c) preheating the filament resistively prior to entrance into the reactor, both in a dry, inert atmosphere and in vacuum, and (d) use of the radioactive brush as well as the preheating technique at the same time. Examination of filament before and after ultrasonic cleaning showed that while what appeared to be soot streaks were removed, certain minor asperities remained unless the intensity of the ultrasonic energy was increased significantly. When such adhesions were removed, they tore part of the basic coating off and made worse defects. Therefore this type of cleaning was not incorporated into the continuous manufacturing unit. With the other cleaning arrangements in line with the deposition reactor, boron filament was prepared under previously determined optimum conditions at various preheater temperatures, nitrogen feed rates and reduced pressures. No improvement in filament average tensile strength or scatter was observed. Values obtained were in the same range as those characteristic of filaments prepared on substrate as received or after storage. Although no positive proof was achieved that

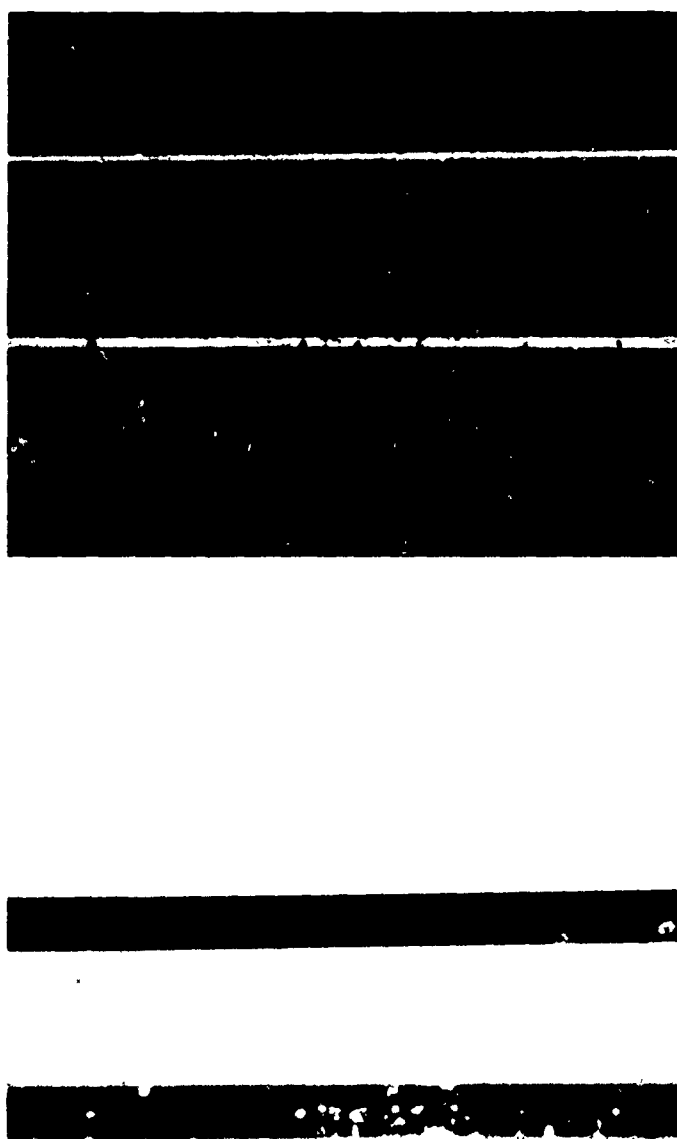


Figure 44. Soot particles on P.C. Coated Silica as Received. Top: Non-polarized Light. Bottom: Polarized Light.

substrate dirt could be eliminated, it appeared to be a less significant factor than had been thought previously, and further efforts at precleaning were dropped, with the exception that the radioactive anti-static brush was left in place as a precaution against laboratory atmospheric dust contamination.

## 2. Electrical Effects

The method used to heat the relatively high resistance carbon coated silica substrate and nascent boron filament involves the use of high voltage transformers connected to the line voltage supply through Variacs, with no external grounding. The occurrence of arcing and sparking at the electrodes had been suspected for some time, and steps were taken to determine positively if indeed this was the case. A high voltage probe was attached to each electrode successively during a routine filament preparation run, and the signal analyzed with a fast response oscilloscope. Figure 45 shows a typical result of these analyses which indicated that intermittent sparking and variations in wave form were occurring. This was particularly pronounced in the higher temperature stages near the end of the reactor where potentials were highest. While the absolute value of the voltage fluctuations are small ( $\sim 50$  V) and their duration is only a few microseconds, if concentrated on a small enough area of the filament, they could be damaging. To eliminate these effects, insulating ceramic guards were placed inside the mercury containing cups to prevent the filament from touching against the steel from which the cups and supports were made. This eliminated not only the intermittent discharges, but also the wave form variation. However, standard filament preparations made with these improvements did not yield filament with less scatter, higher values or without nodules. Examination of fracture surfaces, made throughout this investigation showed that nodules were still associated with failure at low stresses. Average strength values continued to be around 250,000 psi, with low values between 130,000 and 200,000 psi and occasional high values near 350,000 psi. Nevertheless the insulating guards were kept in place during subsequent studies. Other guards were kept in place during subsequent studies. Other random electrical

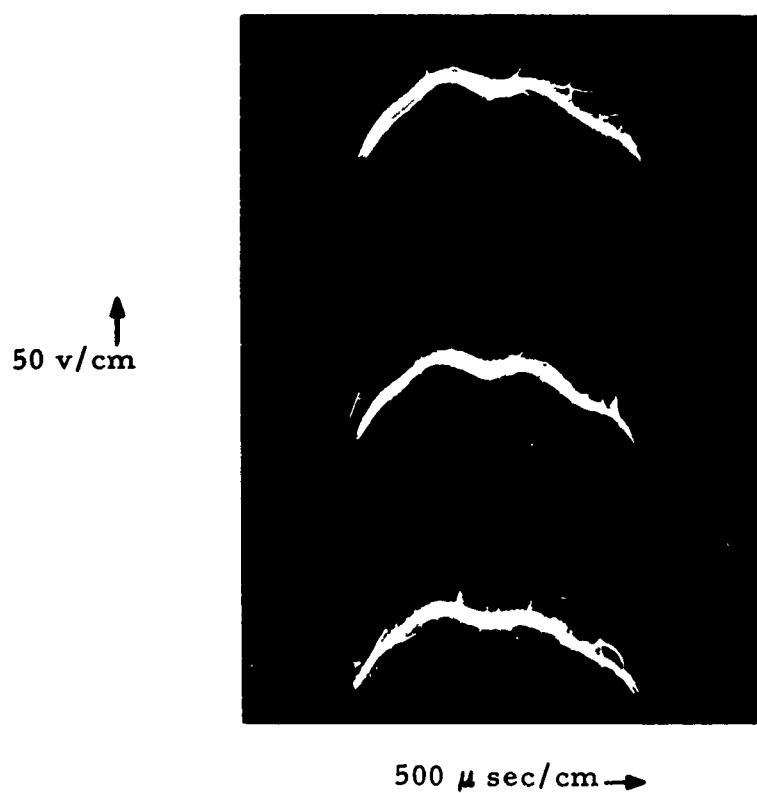


Figure 45. Electrical Discharges at Mercury Electrode.

effects, which were traced down during this period, were occasional sparking in the high voltage transformers due to sharply bent wiring, and damaged coils etc. In general, however, a defective transformer was usually located by occurrence of interaction between various stages during adjustment of a single transformer voltage and probe analysis of the circuit on a continuing basis were not necessary.

### 3. Deposition Effects

The last area for concern, certainly the most likely on the basis of the chemistry of the boranes, lies in the chemistry of diborane: (a) at the filament, (b) in the filament boundary layer, (c) at the mercury surface, (d) at the mercury container walls, and (e) at the reactor wall. Collection of solid debris on the mercury surface has always been observed in this process, but in horizontal laboratory reactors where the standpipe was vertical and the filament did not pass through the central meniscus (see Figure 34), less contamination was observed. In the pilot plant and prototype reactors which were vertically mounted, the filament passed vertically through the center of the mercury cup however, and could entrain some of the solids which would then serve as a nodule nucleus on the filament. The solids that collected on the mercury could have been formed at that location, or collected there having been formed in the gas space immediately above the mercury surface.

As indicated in the list, other deposition effects could lead to dust generated near the filament which could become attached and partially decomposed. The partial decomposition of larger gas phase molecules with a more rapid rate of build-up resulting because of faster reaction with diborane at that site, could also be responsible. The possibility of dust blowing in with the feed gases or through the endcap purge chambers was eliminated by using filters in these lines with little resulting improvement.

Before beginning this series of deposition effect experiments, a 3/4" diameter reactor had been substituted for the 1-1/2" prototype reactor which was used for process studies up to this time. This was done in order to

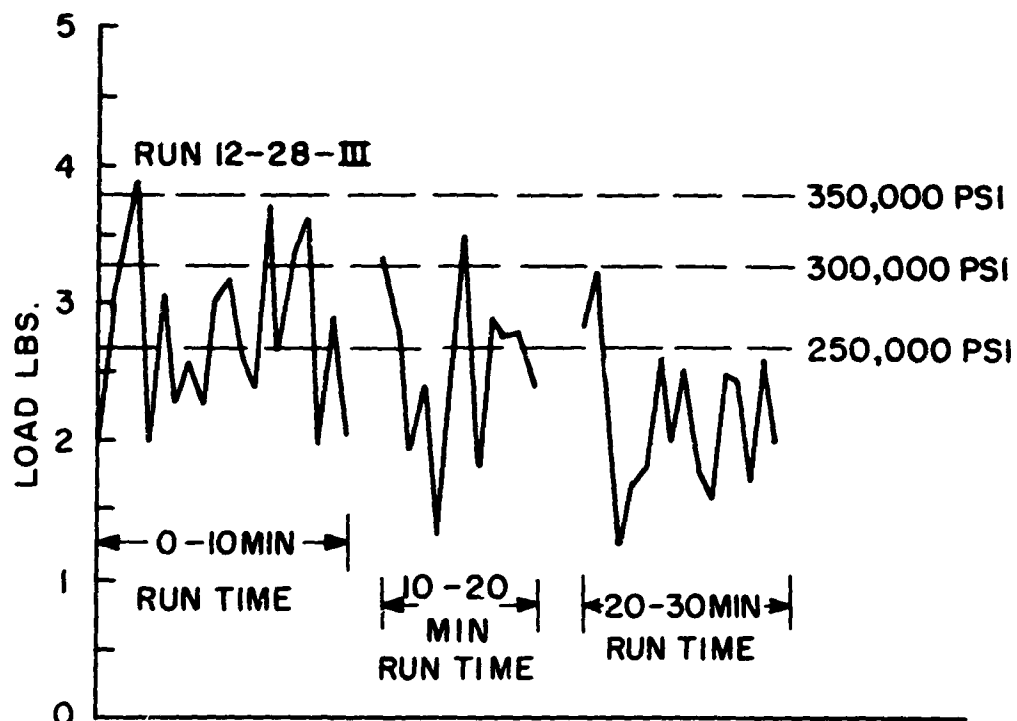
reduce the number of geometry changes between the laboratory and pilot plant reactors and thus prevent confusion in the interpretation of results of deposition experiments designed to reveal the source of nodule producing contamination. The performance of this reactor in the preparation of filaments was characterized by using the optimum conditions developed during the extensive work with a prototype pre-pilot plant reactor earlier in the year. These conditions were varied with respect to pressure, feed rate, and temperature in order to verify the optimum range for each parameter. The results of tensile tests made on the resulting filament showed that the conditions arrived at earlier were indeed those which gave the best average filament strengths. Material prepared at high temperature, high feed rate or pressure with respect to the optimum condition was uniformly extremely weak, so as to be virtually untestable. The situation was similar for material prepared at lower pressure, feed rate, and temperature, although not nearly so pronounced. The principal drawback to operating at these reduced conditions was the low rate of deposition. Table XII lists results for runs made at different temperatures.

Having thus verified a region of operation in which filament could be prepared which was characterized by individual tensile strength values greater than about 350,000 psi, the next task was to eliminate the causes for low strength failure, especially those failures which occurred below 200,000 psi, which appeared frequently enough to reduce the average tensile strength to less than 275,000-280,000 psi, and which would make the filament difficult to process in manufacturing operations.

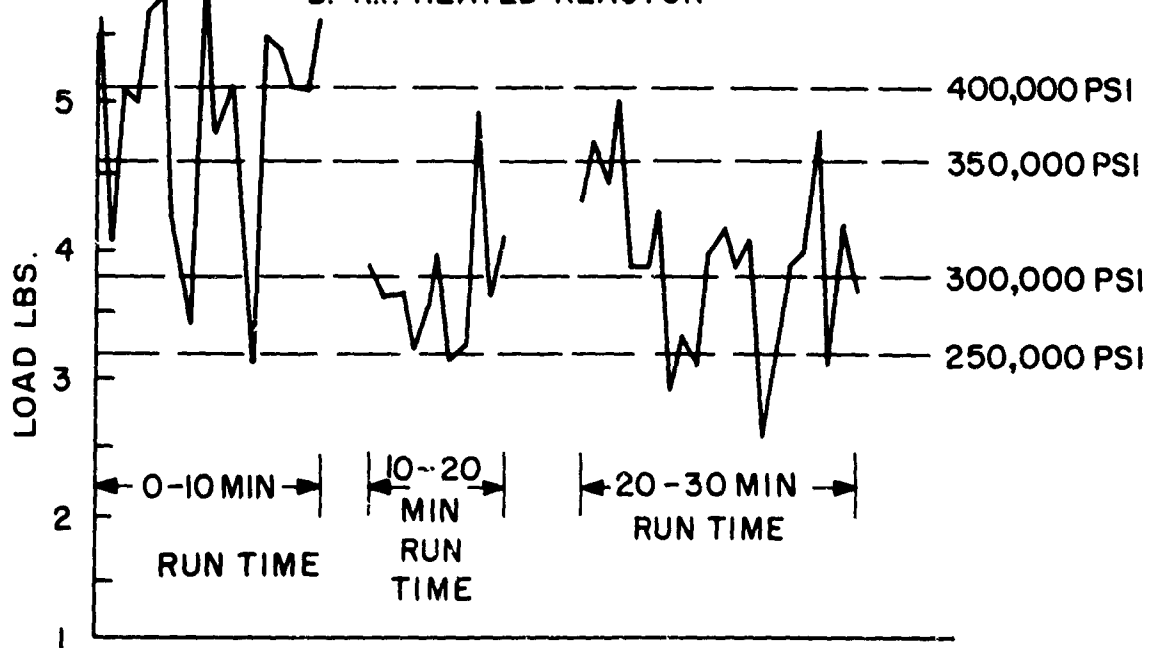
Figure 46 shows the variation prevailing in consecutive filament tests made under these standard conditions: using material taken from the first three 10-minute periods of continuous operation, i. e., from the first 360 feet of filament. These values are representative of material made under these conditions and typify the entire problem of reproducibility and low strength.

During these characterizations runs, exterior reactor wall temperatures were monitored by attaching a thermocouple at each stage adjacent

### A. MERCURY CONTACT REACTOR



### B. R.F. HEATED REACTOR



N302-896

Figure 46. Scatter in tests on consecutive 4" specimens. Time Lapse in Reactor Between 4" Specimens 20 sec. Time Lapse in Substrate Preparation 0.6 msec.

to the electrode. Figure 47 is a plot of representative wall temperatures after 60 minutes of operation while Figure 48 shows the rate of temperature rise for two of the nine stages. Whether this has any significance with respect to filament strength or not is not known. Cooling the walls with a fan had no measurable effect on filament strength. It was also observed that little if any solids accumulated in the 3/4" reactor during operation. This was probably because the walls became too warm for decaborane to settle out and subsequently form yellow solids by gas/solid interaction with diborane and other gaseous boranes passing through. The possibility of accumulated solids on the walls as the cause of nodules was thus ruled out.

A series of so-called sequential runs were made during the optimization of the 3/4" reactor which showed that the principal problem area lay in the higher temperature stages of the reactor. In these runs, each stage was turned on individually and in order, allowing ten minutes of running time between successive additions to the total number of stages. The filament obtained enabled determination of deposition rate and conversion in each stage, strength and modulus tests on filament as a function of diameter, and observation of the filament surface at different periods during its formation. Tables XIII, XIV and Figure 49 show these results as a function of diameter. Modulus values were observed to follow the rule of mixtures for boron and silica. The filament strength obviously decreases as more stages are added to the reactor to increase diameter. Inasmuch as the later stages are operated at a higher temperature, it appeared that either the chemistry, the electrode arrangement in these stages, or an interaction of the two was responsible for the production of poor material which had been strong to begin with. Surface studies also showed increasing amounts of adherent solids and nodules as the diameter was increased by adding more stages (Figure 50).

Attention was next directed toward the role of accumulation of solids on the mercury in the electrodes.



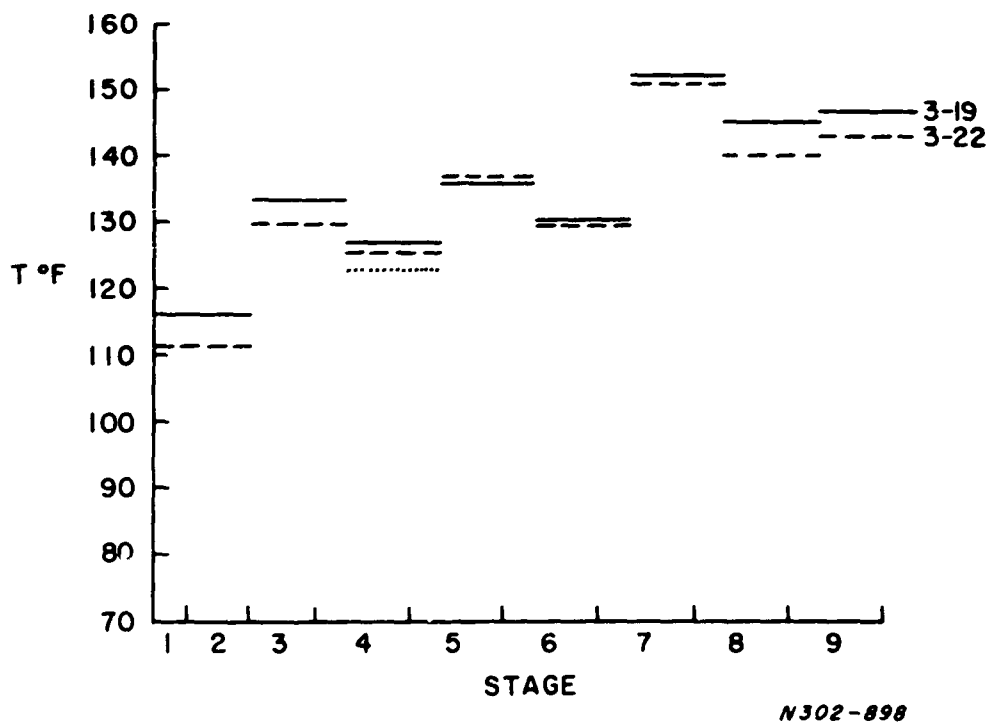


Figure 47. Exterior Wall Temperature of Mercury During Deposition.

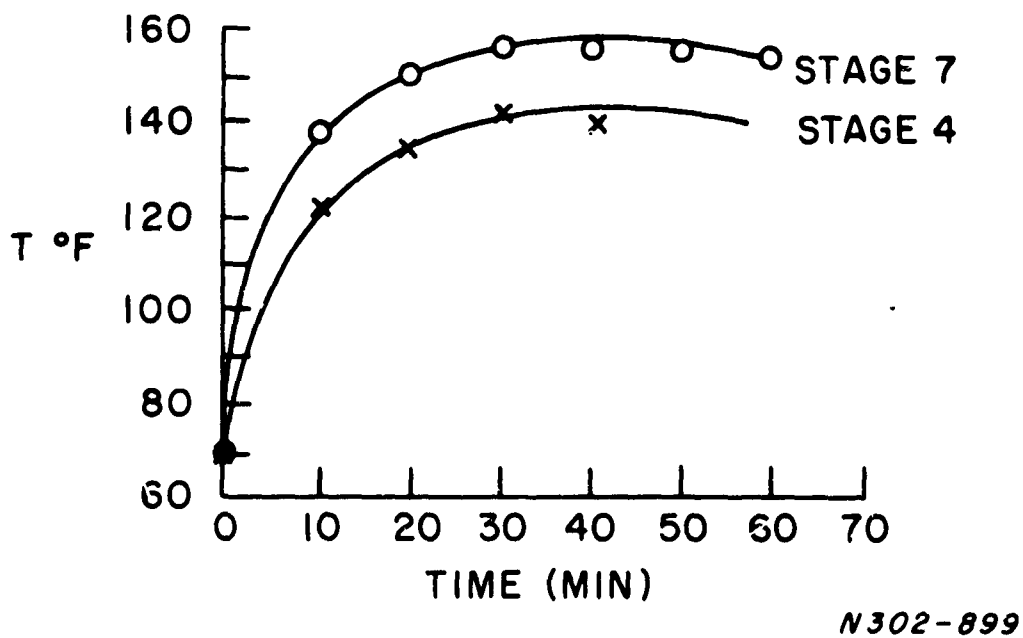


Figure 48. Rate of Wall Temperature Rise.

TABLE XIII  
SEQUENTIAL INITIATION OF MULTISTAGE DEPOSITION

A. Initial Conditions															
			Reactor Pressure			22.5 torr									
			Filament Speed			12.75 fpm									
			Feed Pressure			4 psig									
			Gas Feed Rate			2030 cc/min total (54 cc/min/inch)									
B. Experimental Data															
Time (min.)	Stage	OUTER REACTOR WALL TEMP. (°F)								REACTOR PRESS(torr)	C. Filament Properties				
		1	2	3	4	5	6	7	8		9	DIAMETER MILS	U.T.S. (KSI) Avg. High Low		
0		Right of Line: Stage Not Heated													
10		Left of Line: Stage Heated													
20		85	70	70	70	70	70	70	70	70	22.5	1.0	144	280	51
30		95	105	70	"	"	"	"	"	"	22.5	1.2	137	177	88
40		100	120	110	"	"	"	"	"	"	"	1.5	191	254	119
50		108	127	125	118	"	"	"	"	"	"	1.9	215	296	148
60		110	132	133	134	114	"	"	"	"	"	2.4	257	354	155
70		114	135	136	140	129	119	"	"	"	"	2.75	340	494	168
80		115	135	138	145	136	135	130	"	"	23	3.15	306	394	168
90		114	135	138	145	136	144	150	132	"	24	3.8	277	370	168
105		112	134	135	143	136	145	155	152	150	24.5	4.3	204	200	138
115		* 132	132	140	135	149	160	160	159		24.5	4.2	251	404	137
125		-	134	135	145	140	152	164	160	105	"	4.2	"	"	"
135		-	135	136	148	140	150	158	110	85	23	3.2	249	323	118
145		-	136	138	147	140	148	112	91	79	22.5	2.7	200	411	245
155		-	136	138	146	135	105	92	81	75	"	2.3	345	453	248
163		-	135	135	142	104	88	80	75	73	"	2.0	283	350	229
168		-	135	131	105	86	79	76	74	71	"	1.5	310	370	195
173		-	134	120	98	83	77	75	74	71	"	1.15	265	398	180
		-	112	99	87	79	75	74	73	71	"	1.1	106	117	91
		-	112	99	87	79	75	74	73	71	"	1.0	145	197	102

\* not recorded.

\* not recorded.

TABLE XIV

MODULUS AS FUNCTION OF  
FILAMENT DIAMETER

Diam. (mils)	E $10^6$ psi	Diam. (mils)	E $10^6$ psi
1.0	18.7	1	15.7
1.20	25.7	1.23	29.3
1.40	36.1	1.55	37.7
1.75	40.9	1.87	45.8
2.00	51.1	2.30	48.7
2.50	47.6	2.72	50.8
2.80	51.2	3.57	51.5
3.15	52.4	4.00	52.2
3.65	50.1		
3.85			

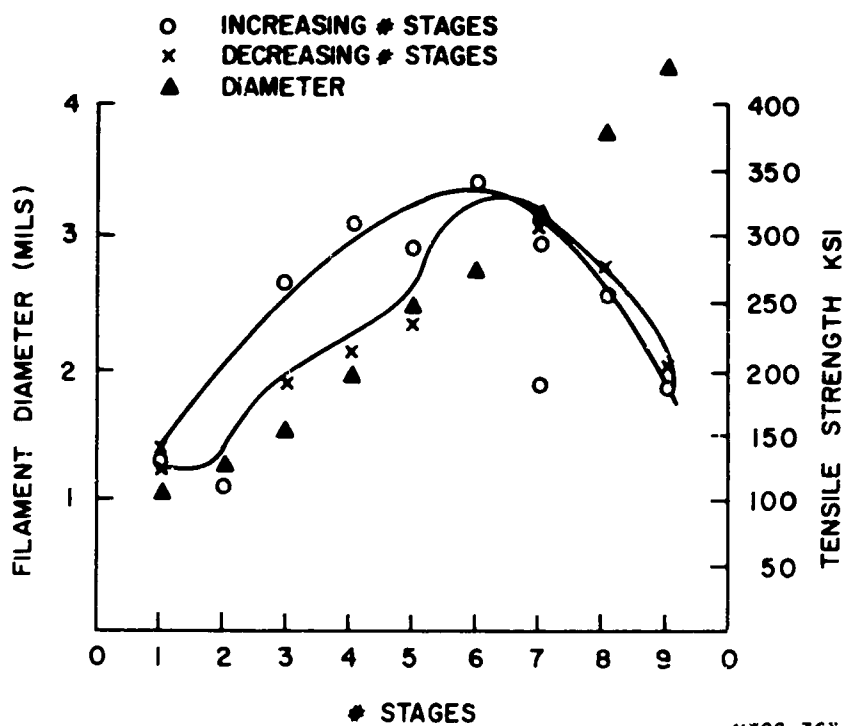


Figure 49. Effect of Increasing Number of Reactor Stages on Strength and Diameter,



A.  
AFTER PASSING  
THROUGH 1ST STAGE.

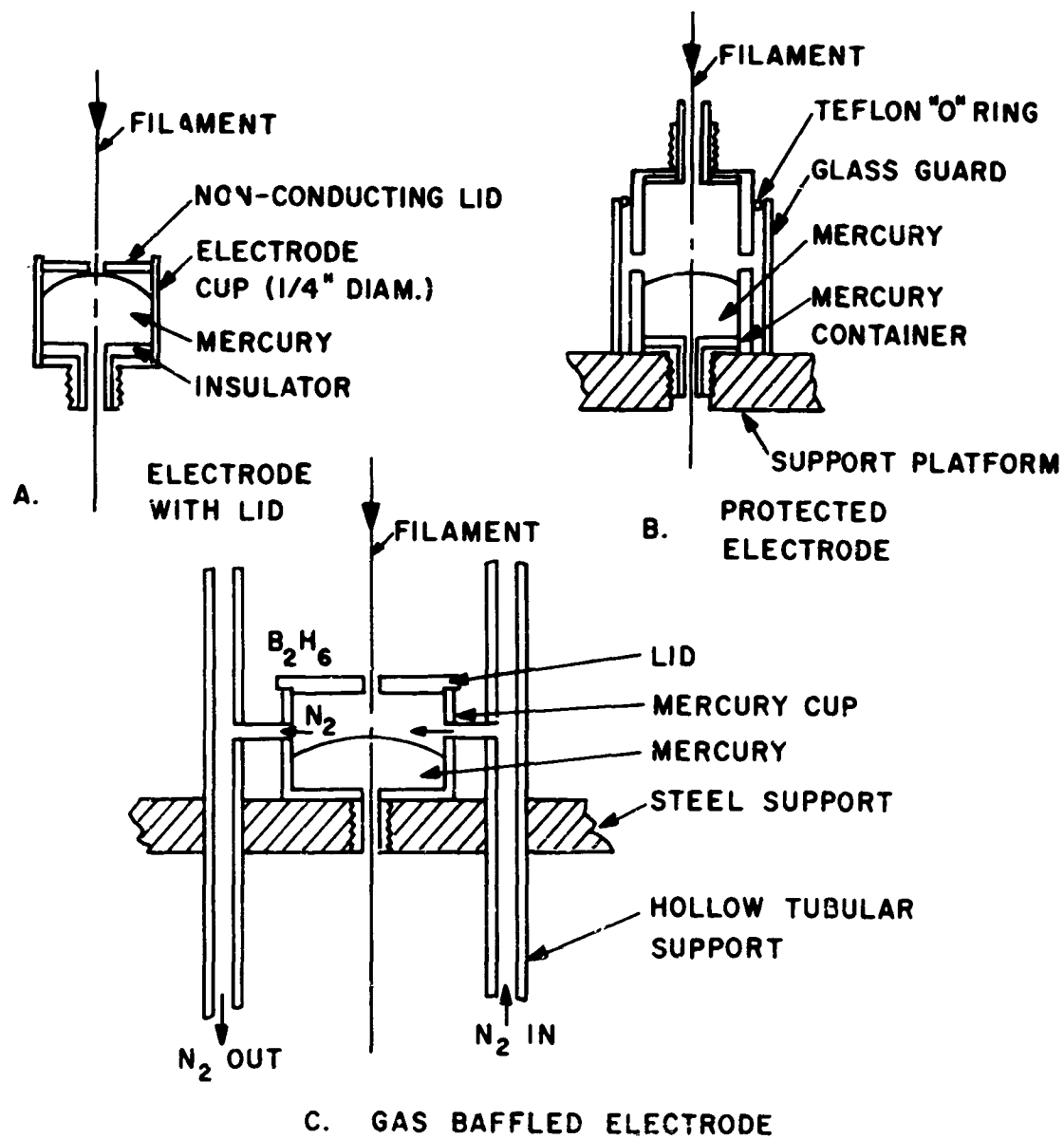


B.  
AFTER PASSING  
THROUGH 9 STAGES.

Figure 50. Surface Contamination on Partially (Upper) and Fully (Lower) Formed Boron Filament (490X).

To prevent the adherence of solids at the electrodes, several design changes were made to prevent diborane from contacting the surface through which the filament had to pass, and to prevent particles formed in the gas phase from settling on the surface. Figure 51 a, b, and c shows schematically three electrode design modifications which are similar in concept in that they attempt to keep diborane away from the mercury. In the first design, a non-conducting lid was placed over the mercury; the filament passed down through a slot in the lid. Results with this design were initially encouraging but after extended running were worse than those obtained with the open cup, primarily because the lid became overheated and served as a polymerization site for diborane. Eventually, it became coated with decaborane and the slot became plugged with solids which adhered to the filament (Figure 52). Average strengths were also lower (see Table XV).

The second modification, shown in Figure 51b consisted of a protected electrode, in which a second empty electrode container was inverted and fitted tightly over the mercury-containing cup as shown. This provided a dead space over the mercury and, in addition, considerably reduced the rate at which the mercury was lost. While in operation, a refluxing action was set up, with mercury evaporating from the region adjacent to the filament, and condensing on the inner walls of the protective cover. In contrast to other electrode designs, the surface of the mercury next to the filament remained clean while solids collected around the edge. Filament prepared with this type of electrode averaged over 300,000 psi as shown in Table XV. The significant aspect of these results is not so much the increase in average strength, however, as the manner in which it was accomplished, i.e., by increasing the value of the low strength failures, as well as decreasing their frequency. However, although low strength failures were not as low as they had been previously, nodules were still a part of the failure mechanism. Subsequent work with this electrode showed that, while it enabled production of filament with strengths averaging over 300,000 psi, it also brought about a higher conversion of diborane to intermediate hydrides because of the larger



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Figure 51. Mercury Electrode Designs

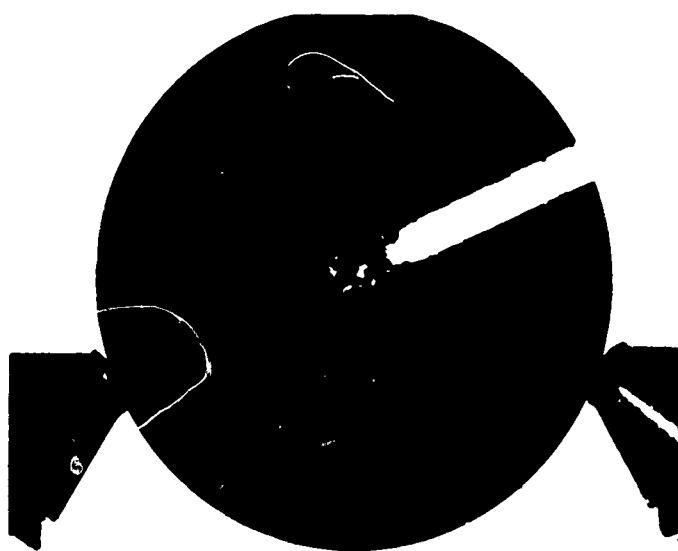


Figure 52. Protective Lid from Mercury Cup Showing Accumulation of Solids in Filament Slot

TABLE XV  
TENSILE STRENGTH (KSI) OF 4.0 MIL FILAMENT PREPARED WITH VARIOUS ELECTRODE DESIGNS

Time After Start (min.)	Open Cup			Cup with Lid			Protected Cup			R-F Heating		
	High	Low	Avg.	High	Low	Avg.	High	Low	Avg.	High	Low	Avg.
+ 0	340	192	273	250	129	206	374	231	294	470	235	371
+ 10	340	266	295	269	149	216	366	159	318	390	263	302
+ 20	329	170	240	268	120	212	398	286	330	398	254	318
+ 30	266	159	207	300	159	235	330	135	282			
+ 40	251	133	199	302	155	226	445	279	330			
+ 50	259	138	215	280	151	206	398	279	334			
+ 60	358	188	273	318	96	191	390	239	310			
+ 70	356	257	306	338	207	258						
+ 80	348	204	275	318	159	215						
+ 90	377	162	304	273	170	231						
+100	397	188	311									
+ 120	431	166	282									
+ 130	363	136	267									



area of hot surface exposed to the gas feed stream. This is discussed in a later section concerned with material balances.

The third modification involved the use of the 1 1/2" reactor because of the nature of the geometry required. The reactor insert, i.e., the spine supporting the ten mercury cups and collimating slots to form the nine reactor stages, was modified to permit an inert gas to be passed across the mercury during deposition. A non-conducting lid was provided, through which the filament passed by means of a 10 mil hole, to prevent the purge gas from mixing with the reactor gas. A separate pumping system was attached to the purge line, effectively making two independent low-pressure gas circulation systems within the same reactor. The pressure in the purge line was adjusted by means of a throttle valve so that it was slightly below operating pressure in the reactor proper. The mercury cup design is shown in Figure 51c. Results obtained with this reactor were unsatisfactory primarily because of the small amount of mercury permitted within the cup after provision had been made for the gas inlet and exhaust ports. The cup quickly became overheated and formation of considerable polymer was noticed early in the run. Because of the larger diameter, the walls were cooler and deposition of solids was possible there also. No tensile strength values were measured because of difficulty in handling the filament. However, the principal appeared to be sound, and an improved design was contemplated too late in the program to be tried.

#### 4. Indirect Filament Heating

Under Task III, radio frequency methods were successfully developed for heating the filament during deposition. Boron filament on carbon-coated silica was prepared in a reactor identical with the mercury prototype reactor to evaluate the potential of this approach to producing high strength material of greater uniformity. Tensile tests of the product were convincing evidence that elimination of the mercury electrodes not only brought a marked increase in strength, but also a decrease in scatter. Average values were on the average more than 50 percent higher, while the occasional low break occurred

at a breaking stress of nearly double that of filament prepared in the mercury contact reactor. Table XV shows a comparison of average, high, and low values obtained with various mercury electrode designs with those obtained in the RF heated reactor. An estimate of the point-to-point scatter can be obtained by comparing the upper and lower portions of Figure 46. The data shown in the lower portion are listed in Table XVI and consist of consecutive tests made on material prepared in the first ten, twenty, and thirty minute portions of a run. A downward trend in the average is visible which is believed to be related to heating up of the reactor walls and collimating plate, an effect which is apparently overridden in the mercury contact reactor by the high degree of borane pyrolysis occurring at the electrodes themselves. The low occasional breaks are still characteristic of a random effect, perhaps associated with gas phase soot or with growth variations.

Further ramifications of this method of heating are discussed below in conjunction with some design considerations of a high speed reactor. At this point, it is sufficient to say that the use of RF heating effectively eliminated the difficulties with mercury electrodes and the contamination, arcing, and maintenance problems associated with them.

TABLE XVI

CONSECUTIVE TENSILE TEST RESULTS FOR  
BORON/SiO<sub>2</sub> FILAMENT PREPARED BY RF HEATING

Time	Strength (KSI)
0-10	424, 311, 386, 379, 432, 440, 303, 258, 462, 364, 386, 333, 235, 418, 410, 386, 386, 424
10-20	310, 294, 294, 263, 286, 334, 271, 279, 390, 286, 310,
20-30	342, 374, 350, 398, 302, 302, 334, 231, 271, 254, 318, 334, 310, 326, 215, 263, 310, 318, 390, 254, 334, 294, 215, 366

Typical Modulus Values: 51.5, 52.5 x 10<sup>6</sup> psi

## 5. Summary

The experiments conducted with the goal of improving the quality and constancy of properties in boron filament prepared from diborane led to the following important conclusions:

(1) Low tensile strength values and high scatter are associated with the random and accidental formation of nodules on the filament. These are stress raisers which can lower the average strength of this brittle surface sensitive material by 50% or more, depending on the size distribution and frequency of the nodules.

(2) The primary cause for nodule formation is the adherence of solid particles by the filament as it passes through the mercury electrodes. These solid particles become the nodule nuclei in the succeeding stages

(3) The severity of this effect increases with the diameter of the filament principally because the greatest buildup of material takes place in the final three or four stages of deposition where temperatures are highest and the probability of forming higher molecular weight hydride solids on the contacts is greatest. Filament prepared in sequential deposition runs, in which successive stages are lit up in sequence showed that filament strength increases up to the fifth stage, at which time a pronounced decline takes place as filament diameter increases. Surface studies of filament issuing from each of the stages, as if it were the final stage, showed the presence of increasing amounts of adherent solids as the filament progressed through the reactor.

(4) Progressively more successful efforts to minimize contamination of the electrodes by electrode design changes were eventually rewarded by production of filament with average strengths in excess of 300,000 psi. Scatter was still a dominant factor, however. Maintenance problems in a large manufacturing facility under such circumstances would become difficult and expensive in terms of down time and labor costs since all of the improved designs eventually became contaminated to some extent resulting in a falling off of average tensile strength.

(5) The most successful solution to the problem of non-uniformity and low strength was the use of radio frequency heating which eliminated the principal source of the trouble, the mercury electrodes.

#### F. FILAMENT MORPHOLOGY

Considerable reference has been made in the previous sections to nodules and nodule forming conditions. The need to understand the origins of these nodules and the conditions which produce them become evident through a simultaneous and continuing series of observations made on the filament produced in each run. Interpretation of the results of each run was based as much on the appearance of the resulting filament in general, and on a large number of individual fracture surfaces at all stress levels at which observations were possible.

A characteristic of boron filaments with a silica core is the relatively smooth though somewhat grainy exterior, compared with the corn-cob structure of boron filaments with a tungsten core (Figure 53). However, at random sites along the filament, the smooth structure is punctuated by small, isolated nodules of varying diameter and height. Figure 41 is an example of these general aspects of the appearance of the filament, while Figure 40 shows the influence of the nodule on failure. Because the edge of the nodule is usually tangent to the failure plane, its significance was not sufficiently recognized at first. With the accumulation of additional views of fracture surfaces, however, it became evident that the presence of the nodule was a weakening factor that caused premature failure by virtue of its stress concentrating effect. In several isolated cases, failure through a nodule was observed which thus offered the opportunity to view the origin of the nodule directly, rather than after a tedious and uncertain etching away of the failure surface from the tangent of the nodule to its center.

Figures 54, 55 and 56 are photomicrographs of such a situation in which the center of the nodule has been exposed. It is evident that the foreign body which serves as the core of the nodule became attached between stages 2 and 3. These were obtained rather late in the study of sources of nodules, after

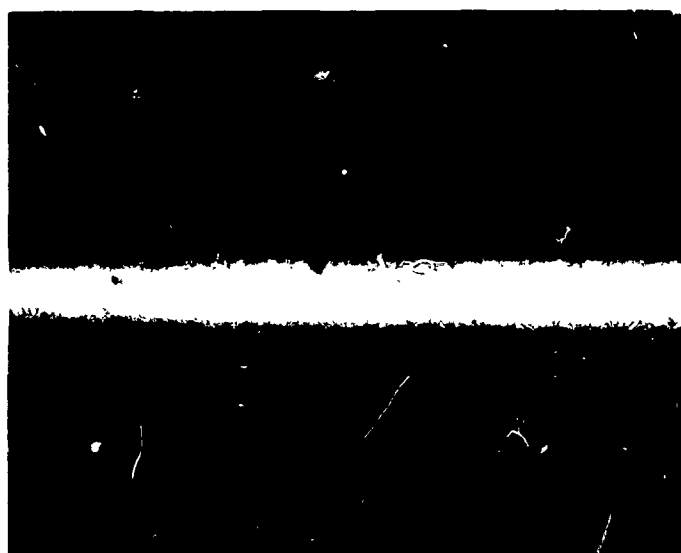


Figure 53. Appearance of Boron Filament Deposited on Silica (490X)

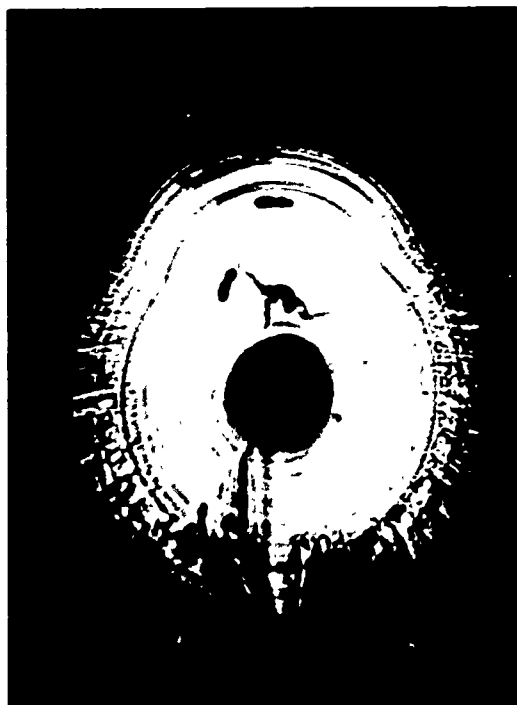


A.



B.

Matching surfaces of failure through nodule showing nodule nucleus. Failure occurred at 159 Ksi in filament with average  $\sigma = 318$  Ksi. Additional markings on side A are dust particles. Diam through nodule is 4.37 mils, through minor axis = 3.98 mils (593X)



C.

Figure 54. Side B after etching 15 min. in conc.  $H_2O_2$ , showing nodule source and etched out hydrogen-rich regions (see text) 593X



**Figure 55. Fully Formed (4 Mil) Boron Filament Showing External Nodule and Source Near Substrate at About  $350^{\circ}$  from Top Center (593X).**



A.



B.



C.

Figure 56. Transverse View of Fracture Surface of B/SiO<sub>2</sub> Filament Prepared by RF Heating. Failure occurred at 458,000 psi, originating at the Core (Sheath Interface Shown in A (1210X). B. Unetched View (593X). C. After Etching 1/2 hr. (593X))



it had already been concluded that the principal contributing factor was solids deposited on the mercury surfaces. Figure 56 is another example of this, as is also Figure 50 which shows how the product of each deposition stage can carry into the next stage the origins of the nodules to be formed and enlarged from that point on.

An important point to be noted is that the area of the nodule is not as important in behavior as the height of the nodule, or perhaps the ratio of height to area, i.e., its aspect ratio. The greater this ratio, the more severe the concentration of stress appeared to be, although it was not possible to place this observation on a quantitative basis. Circumstantial evidence supporting this, however, was obtained in examinations of filament prepared in the RF heated deposition reactor. Failure in this filament is not always associated with a nodule, particularly at high values, nor is the origin of failure always at the filament outer surface. Figure 56 shows various views of the fracture surface of a 4.1 mil dia. filament which failed at a load of 6.1 lb. (454,000 psi) in which it is evident that failure started at the core/deposit interface where residual tensile stress is greatest and that shattering of the filament due to the sudden release of stored energy did not occur, which is of course responsible for the relatively flat fracture surface. Rather large but flat nodules existed within the gauge length and yet failure did not occur there (Figure 43). These observations have not been universal with filament prepared in the RF heated reactor, but they have not been seen at all on material made in direct resistance heated reactors. It would appear to imply that different residual stress patterns exist in these two materials which produce differing failure phenomena. No further detailed studies have been made of these phenomena, although the method of heating may be a contributing factor.

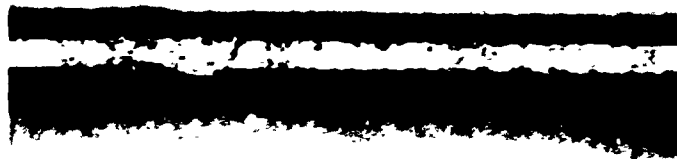
In addition to the appearance of a nodule nucleus in Figure 54a etching with peroxide revealed the presence of what appeared to have been "soft" spots in the filament, seen in Figure 54c, which were not visible before etching. These may be explained by the rapidity of deposition and the strong

possibility that soft agglomerates of higher hydrides picked up at an electrode were melted and only partially decomposed before being covered with a layer of hard, brittle boron, trapping them inside. Such regions are also potential sources of weakness in the absence of an even weaker segment in the gage length, such as a nodule, and their presence serves to explain occasional low strength failures in the absence of a nodule, as well as rings of easily etched material which separates each deposition stage contribution to the total filament. Nearly all of the filament produced in either direct contact or RF heated reactors bears a "snake skin" pattern on its outer surface which is easily washed off with acetone. Figure 57 shows before and after views of this.

Where filament is suspected of containing some undecomposed higher hydrides (Figure 55), a measurable hydrogen content can be anticipated. The hydrogen is most probably concentrated at the rings where the contamination is accumulated and subsequently trapped in the deposit. Specimens of material made in different runs were submitted to the General Electric Large Steam Turbine and Generator Materials and Processes Laboratory, Schenectady, New York, for hydrogen analysis by vacuum fusion. Values of 0.036, 0.049 and 0.056 weight percent hydrogen (corrected for core hydrogen content) were obtained for runs made at progressively decreasing power settings (temperature). These values are in line with previous determinations and the trend is compatible with the borane pyrolysis rationale presently accepted.

#### G. PROCESS CHEMISTRY AND MATERIAL BALANCE

To develop a successful commercial process it is essential that an understanding of the process chemistry under production conditions be combined with analytical data to arrive at a reliable estimate of the material balance and materials costs in process equipment under production conditions. During the final phases of the work described in this report, an analytical system was set up to obtain this information, as is detailed in Appendix A.



A.



B.



C.

Figure 57. Soft Adherent Material or Stains on Outer Filament Surface After Passing Through the First (View A) and Last (View B) Electrodes. Shown in C is the Filament in B After Wiping With Acetone (All Magnifications at 490X).

As has been pointed out earlier, the thermal decomposition of diborane and to boron in making boron filament leads to the production of the following by-products: hydrogen, tetraborane-10, pentaborane-9, pentaborane-11, decaborane-14 and higher molecular weight hydrides collectively termed yellow solids. The feed gas consisted largely of diborane with traces of tetraborane and pentaborane-9, large or small depending on purity, previous history and feed stock temperature; hydrogen was also present on occasion, but was bled off prior to filament preparation. This was done because of its negative influence on deposition rate and strength shown in Table XVII which summarizes results obtained in deposition experiments carried out with mixtures of diborane and hydrogen and diborane and helium.

TABLE XVII

EFFECT OF HYDROGEN ON DEPOSITION RATE AND STRENGTH

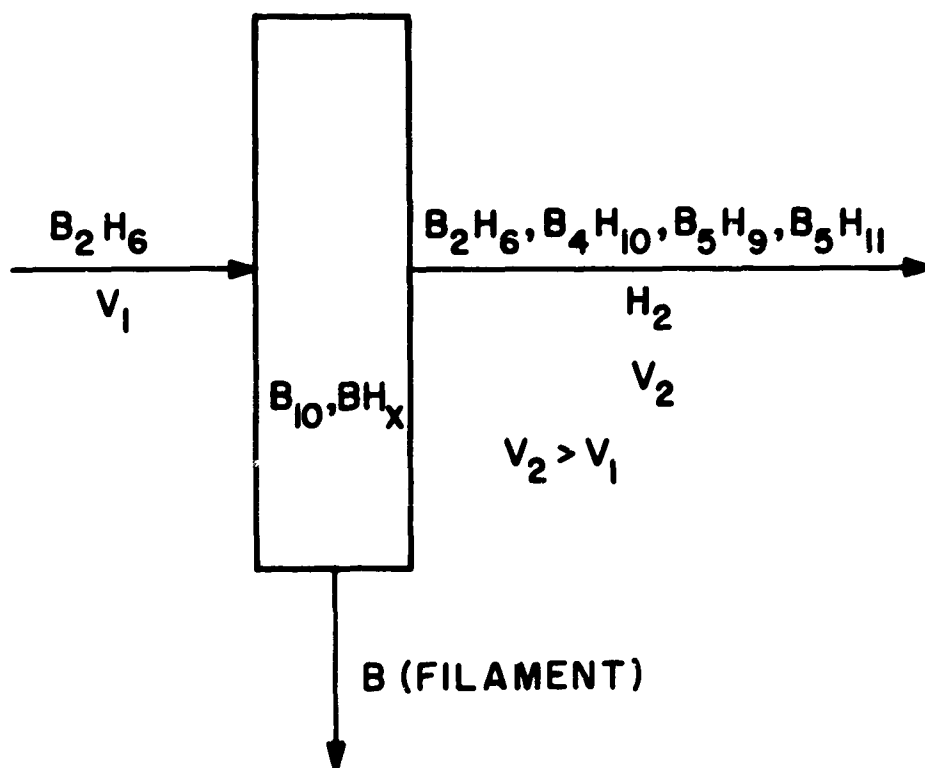
<u>Diborane Flow (cc/in/min)</u>	<u>Additive</u>	<u>Additive Flow (cc/in/min)</u>	<u>Final Diam. (mils)</u>	<u>Avg. Tensile Strength (Kpsi)</u>	<u>Temp. Range (°C)</u>
25	--	--	3.9	193	700-750
25	H <sub>2</sub>	5(20%)	3.65	142	700-750
25	--	--	3.9	203	700-750
25	H <sub>2</sub>	10(40%)	3.5	115	700-750
25	--	--	3.7	153	700-750
25	He	5(20%)	3.6	122	700-750
25	--	--	4.1	182	800-850
25	H <sub>2</sub>	5(20%)	3.7	130	800-850

The exhaust gas consisted largely of varying amounts of unreacted diborane, hydrogen and the gaseous intermediates, tetraborane-10, pentaborane-9, and pentaborane-11. Traces of decaborane were also detected in the exhaust gas on occasion, but in amounts too small to be measured. Decaborane and yellow solids remained largely in the exhaust lines leading from the reactor where it could not be recovered, while solid boron left the reactor

as filament. A material balance of this system must take into account all of these boron values, which are summarized in the chart shown in Figure 58. A serious complicating factor in arriving at a material balance by analysis of the feed and exhaust gas streams was the change in volume of gas which resulted from the interactions in the reactor. Although the feed gas was metered into the reactor through a flowmeter at a known backpressure, the exhaust gas left the reactor at low pressure and had a variable composition which depended on the degree of conversion to the various by-products. A flowmeter was installed in the exhaust line, the calibration of which, however, was of questionable value because it only indicates the volume of gaseous effluents. Consequently, indirect approaches to defining the volume change occurring in the reactor were resorted to. These were based on the fact that all borane condensation reactions of consequence in this process result in an increase in gas volume, and the observation that excessive quantities of solids did not usually appear in the process lines and reactor compared to the total amount of diborane fed. These internal analytical considerations are discussed in Appendix B where typical material balance calculations are also shown. The discussion which follows here is based on what is believed to be the best compromise of experience, observation and judgement in arriving at an exhaust gas volume in each case which gave consistent and believable balances.

#### 1. Reactor Design and Process Chemistry

It was briefly mentioned earlier that reactor design considerations are important because of the sensitivity of diborane to heated surfaces and thermal gradients. In most mercury electrode reactors used for process studies, there are three reaction sites where formation of borane intermediates and polymer occurs. These are the mercury electrode complex, the reactor walls, and the heated gas phase boundary layer adjacent to the filament on which boron is formed. The filament surface presumably is hot enough to cause diborane to fragment rather than condense; however, higher molecular weight hydrides may strike the filament and not decompose completely because of their greater stability, but rather react with diborane as it approaches the surface.



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Figure 58. Schematic Representation of Material Balance Components.

The consequences of formation of intermediate hydrides are mainly economic. Since the solid products cannot be recycled, they constitute a materials loss to the process; the vapor phase intermediates may or may not be able to be used again but, in either case, they could raise a material handling problem inasmuch as they can react further with diborane to form solids and hydrogen in the process streams, traps, etc. At present, it is not clear whether a certain small amount of these intermediates is required to make the best filament. In the light of the present work it does not appear to be possible to avoid forming at least this much.

The analytical procedure was used in a number of filament preparation runs in which certain modifications had been made in either reactor design or deposition procedure. The influence of these changes on the material balance and gas composition was evident; it was also possible to observe variations in gas composition in the reactor as the filament proceeded from the first to the last stage, becoming thicker and hotter as it did so. Table XVIII shows the variation in gas composition in a 3/4" O.D. reactor under so-called optimum conditions which were developed earlier in the program using filament tensile strength as the response to process parameter variations. From this it is seen that the borane gas phase pyrolysis follows the general trends observed heretofore, i. e. at lower temperatures formation of the lower molecular weight is favored, while at higher temperatures, the more stable pentaborane-9, predominates among the by-products. Changes in filament temperature within a single stage produced the same trend, as is shown in Table XIX, although it is not as clear cut because of the thermal inertia of the massive electrode supports. Cooling the reactor walls with a fan during deposition did not greatly reduce the extent of intermediate formation even though the walls approached 70°C in the higher temperature stages (Figures 47 and 48).

Variation in electrode design affected the concentration of by-products to some extent as is shown in Table XX, which compares the exhaust gas composition in runs where two mercury electrode designs and RF heating were used.

The protected electrode (shown in Figure 51), although it kept the mercury clean and led to better filament, was larger and caused larger amounts of the intermediate deposits to form. Unfortunately, there was no opportunity to repeat the optimization studies in these reactors so that the effects of pressure and feed rate changes could also be studied. Despite the total absence of hot electrodes, intermediates are formed in the RF heated reactor, possibly at the collimating plate, but more likely in the gas phase around the filament.

TABLE XVIII

VARIATION IN GAS COMPOSITION AT POINTS ALONG THE  
FILAMENT DURING DEPOSITION AT STANDARD  
CONDITIONS

<u>Stage</u>	<u>Mole Percent</u>				
	<u>B<sub>2</sub>H<sub>6</sub></u>	<u>B<sub>6</sub>H<sub>10</sub></u>	<u>B<sub>5</sub>H<sub>9</sub></u>	<u>B<sub>5</sub>H<sub>11</sub></u>	<u>H<sub>2</sub></u>
1	95.5	0.25	0.11	0.06	4.16
2	97.6	0.25	0.11	0.03	2.04
3	94.0	0.31	0.24	0.08	5.41
4	96.2	0.27	0.16	0.08	3.34
5	92.0	0.37	0.39	0.14	13.80
6	86.9	0.41	0.50	0.14	12.20
7	84.0	0.44	0.71	0.14	14.90
8	82.5	0.52	0.85	0.09	16.20
9	78.5	0.55	0.88	0.06	20.10

Exhaust Gas

At Equilibrium	88.9	0.38	0.67	0.9	9.82
At Beginning	86.9	0.69	0.56	0	12.00
With Cooled Wall	89.5	0.31	0.50	0.23	9.54



TABLE XIX

**VARIATION IN GAS COMPOSITION WITH CHANGE IN  
FILAMENT TEMPERATURE (POWER VARIATIONS)**

**A. TOTAL GAS COMPOSITION, STAGE 8 ONLY**

**1. Standard Deposition Conditions Mole %**

No.	$B_2H_6$	$B_4H_{10}$	$B_5H_9$	$B_5H_{11}$	$H_2$
1	74.6	0.29	0.95	0.36	23.80
2	78.5	0.24	1.47	0.46	19.40
3	78.5	0.24	1.52	0.49	20.00

**2. At Lower Temperature (20% Power Reduction)**

No.	$B_2H_6$	$B_4H_{10}$	$B_5H_9$	$B_5H_{11}$	$H_2$
1	86.8	0.19	1.22	0.49	11.44
2	81.5	0.17	1.14	0.46	16.70

**B. INTERMEDIATE HYDRIDE CONTENT, STAGES 7-9**

Stage	7			8			9		
% Decrease in Power	Mole %			Mole %			Mole %		
	$B_4H_{10}$	$B_5H_9$	$B_5H_{11}$	$B_4H_{10}$	$B_5H_9$	$B_5H_{11}$	$B_4H_{10}$	$B_5H_9$	$B_5H_{11}$
0	.44	.71	.14	.52	.85	.19	.55	--	.06
10	.54	.48	.22	.41	.67	.21	.43	--	.29
20	.76	.43	.20	.53	.54	.29	.34	--	.31
30	.45	.20	.23	.63	.50	.29	--	--	--

TABLE XX

**VARIATION IN EXHAUST GAS COMPOSITION  
WITH ELECTRODE DESIGN**

	Mole Percent				
	$B_2H_6$	$B_4H_{10}$	$B_5H_9$	$B_5H_{11}$	$H_2$
Open Cup	88.9	0.38	0.67	0.17	9.82
Protected Cup	82.1	0.33	0.96	0.28	16.38
RF Heating	93.5	0.18	0.43	0.14	5.8

## 2. Material Balance

The most important contribution of the chromatograph studies was the achievement of a fairly good material balance, and an estimate of the diborane required to form a pound of filament, a basic value required for an economic analysis of the process. Table XXI shows these results, with and without re-cycle in several reaction systems. The RF heated reactor at first appeared to be more efficient since a smaller conversion to intermediates was observed. However, diameter was smaller at equivalent draw speeds, indicating that a lower deposition temperature could have been responsible for the smaller amounts of by-products. This being the case, the absence of the electrodes would appear to be of minor importance to the formation of by products; the primary site for these reactions would then be pinned down to the hot gas envelope surrounding the filament.

On the whole, the estimates of diborane required per pound of filament seem within reason for an economical process. The general range of values, 2-3.5 pounds of diborane per pound of filament, was also verified in one run in which a direct weight balance was obtained of material used and recovered. This is also shown in Table XXI. Recycling the intermediates would lead to savings dependent on the reactor system design. In the case of the protected electrode reactor, for example, Run 3-20, Table XXI, a much larger loss to by products was encountered because of the larger and hotter electrode. Therefore, the material usage without re-cycle was 5.4 pounds of diborane per pound of filament rather than about 3.5 as it was for the open cup electrode system.

The absolute concentration of intermediates is quite low as can be seen in Table XVIII and might not constitute the handling problem referred to earlier. Removal of hydrogen on the other hand is essential. If the recovered by-products were to be stored and continued to react as they are wont to do, their most serious effect would be to generate hydrogen which would have to be removed. A continuous re-cycle on the other hand, assuming hydrogen could be removed in stream, would not appear to offer difficulty

TABLE XXI

MATERIAL BALANCE FOR CONVERSION TO FILAMENT

	Percent Conversion per Pass to Filament	Lbs. B <sub>2</sub> H <sub>6</sub> /lb. Fila- ment Recycle	Lbs. B <sub>2</sub> H <sub>6</sub> /lb. Fila- ment No Recycle	%B <sub>2</sub> H <sub>6</sub> Recovery as B <sub>2</sub> H <sub>6</sub>	Diameter (mils)
Run 2-27 Open Cup Electrodes	2.5	1.9	3.3	93	4.0
Run 2-27 Direct Weighing	2.5	--	4.2	--	4.0
Run 3-20 Protected Electrodes	1.9	3.1	5.6	91.5	3.6
RF Heating Average of 13 Runs	1.8	2.0	3.1	95.5	3.8-4.0

\*Slower filament draw speed

in terms of effect on the filament at low intermediate concentrations. Several experiments were done in which the tetraborane content in the feed gas was about the same as that in the exhaust. Little additional build-up of tetraborane occurred, but it is not known if more solids formed as a result, since required analytical data were not available. Pentaborane-9 was also used as a feed gas additive in minor amounts with no detectable effect. Since it is more stable, however, a build-up of  $B_5H_9$  might be anticipated as well as formation of excessive solids. The problem of what to do with these by-products would have to be solved on the basis of the cost of removing them versus the troubles inherent in trying to re-use them. A compromise is more easily envisioned in which their concentration would be reduced to some significant but non-troublesome level, with the remainder being disposed of periodically. Decaborane on the other hand could be recovered during reactor cleanup operations and might have some resale value depending on the need. Yellow solids form from decaborane and diborane and, if the decaborane recovery is a significant economic benefit, more frequent reactor cleanup might be required.

Changes in reactor design should be in the direction of limiting the number of heated areas and the filament boundary layer thickness to minimize formation of intermediate by-products. Changes in process parameters, assuming filament strength can be retained, should also enable reduction of intermediate hydride formation and therefore of the diborane requirement. In attempting to do this, it is necessary to recall that formation of intermediates and of filament are to a large extent independent of each other, i. e., the formation of boron is not the end result, nor a part of the reaction scheme by which the by-products are formed. The two processes are related by the temperature of deposition and the proximity of the reactive envelope and the substrate. If filament speed must be reduced to achieve a 4.0 mil filament on account of a more desirable low temperature deposition schedule, for formation of intermediates will not necessarily be reduced to the same extent. Thus, efficiency is decreased. This result is seen in Table XXI where, although lower concentrations of intermediates formed in the gas stream using

the RF heated reactor the overall efficiency was not improved because filament speed and hence production rate was also lower. Conversely, if deposition temperatures are raised, the reactive gas envelope will increase in volume and, without significantly reducing the number of gas phase collisions (by lowering pressure or increasing gas velocity for example), the degree of conversion to by-products will also increase. Since the energy requirements for hydride interconversions are nominal compared with the energy of dissociation of diborane, it would appear that attempting to raise production efficiency by this route would be difficult.

#### H. IMPLICATIONS OF RADIO FREQUENCY HEATING IN HIGH SPEED FILAMENT PRODUCTION

Some comments as to the value of RF heating are especially appropriate in the Task IV discussion because of its importance in achieving a high strength relatively uniform product, the basic requirement for any further developments in this field.

As has been pointed out earlier, the primary purpose of Phase I of this program has been the establishment of criteria concerning various aspects of the boron deposition system to enable a high-speed filament reactor to be designed and built. Areas of primary interest have been glass drawing, conductive coating, methods of heating, and process and product improvement. The innovations and improvements in processing and product properties made possible by the development of RF heating have an impact in all of these areas directly or indirectly. Of particular importance is the elimination of the need for a direct electrical contact, liquid or solid, moving or static. In view of the complex low temperature chemistry of the borane system, this has greatly simplified the engineering design and maintenance of a reactor operating at any speed, but much more so for a high speed reactor. The implications with respect to product quality and uniformity have already been noted in preceding sections, regardless of the nature of the conductive coating. Since considerable difficulty had been experienced in the area of making a direct electrical contact to the bare substrate as it entered the reactor, the use of RF heating is of particular value at this point,

inasmuch as it reduces the stringent requirements for uniformity in resistance and for complete continuity of the conductive coating whatever it might be. These considerations apply to the heating of any moving filament in a reactive environment.

In terms of its application to a high speed production reactor, RF heating permits alternatives in design which would not be easily achieved with conventional electrical heating. One basic alternate approach to a high productivity system is the use of multiple filaments within a single reactor. Although this was not the initial concept, it is worthwhile to point out that a number of filaments have been heated to uniform temperature within a single enclosure under somewhat adverse conditions, i.e., in air. Figure 59 shows two views of a demonstration of this capability, which opens up the way to a number of compact multiple filament designs, operating at speeds reduced proportionately to the increase in number of filaments.

It is not the purpose of this section, however, to suggest design methods for multiple filament reactors, but rather to indicate how the method of RF heating can be of value in designing a single high speed filament reactor. Some of these advantages are:

1. No electrodes are required. Thus, there are no heat sinks such as massive electrodes to soak up power and become hot enough to cause side reactions. Threading of the reactor becomes essentially simpler since the internal geometry, without electrodes, is essentially reduced to a hollow cylinder or channel.
2. Direct contact with the apparatus is not required. The possible necessity for water cooling or air cooling of internal reactor components can be met without the need for cumbersome and treacherous vacuum to water and electrical lead-through fittings.
3. The power requirements are extremely low since none is used to heat electrodes. Therefore, a number of reactor coil assemblies can be energized from the same power supply. Reactor length can be varied without affecting the power supply.



Figure 59. Light and Dark Views of Three Boron/SiO<sub>2</sub> Filaments Heated in Air by Induction.

4. Variations in coil spacing can be readily accomplished from the outside without requiring a new reactor shell for each change in stage length. At high speeds, there may well be no need for the coils to be numerous and closely spaced.
5. There is no limit on reactor configuration or orientation, nor is there excessive friction or tension applied to the filament other than what is required to guide it.

Some of these advantages are apparent in the high speed reactor concepts discussed later in this report.

## I. SUMMARY

Variations in tensile strength of filament produced by decomposition of diborane were found to be due to isolated nodules which formed on the filament during production. The source of the nodules was traced to the mercury electrodes which served as secondary reaction sites for production of borane solids. The degree of reaction at the electrodes was determined by their temperatures, higher in the latter reactor stages, and accounted for a deterioration in filament strength with increasing diameter. Methods for alleviating the problem in conventional mercury electrode reactors consisted of protecting the electrodes from the reactive gas mixtures by suitable covers. The most satisfactory method for preventing such effects lay in the complete elimination of the electrodes. This was accomplished by the successful development of a radio frequency method of heating the filament, which resulted in the production of reasonably high strength, uniform filament, having few nodules of any significant stress concentrating effect.

Development of an in-stream analytical system, based on gas chromatographic analysis for diborane, tetraborane-10, pentaborane-9, and pentaborane-11 permitted determination of material balances for a number of different reactor designs. Results indicated that between 1.9 and 3.5 pounds of diborane would be required to produce one pound of filament, and that the intermediate hydride concentration in the gas phase was less than one mole percent. The effects of varying process parameters and reactor design on material balance and by-product generation were also studied briefly and the



results give valuable clues as to future optimum reactor design, as well as for gas recovery and handling on a large scale.

Insufficient time was available for completely studying the methods for increasing deposition rate in the hydride system using the radio frequency heating approach in conjunction with the analytical studies. Efforts to increase deposition rate by first depositing a layer of boron on the carbon coated silica substrate from a halide system were not initially successful enough to warrant further intensive study.

## SECTION VI

### TASK IVB - IN-LINE RESIN COATING OF BORON FILAMENTS

**Objective:** To assess the value of and to provide immediate resin coating onto boron filament before admission into the atmosphere if desirable, to increase the bonding between filaments and matrix, and to improve filament spacing in composites

#### A. BACKGROUND

The desirability of applying a protective coating to the boron surface before it emerges into the atmosphere arose from studies sponsored by the Air Force Materials Laboratory as discussed, for example, in Ref. 9. In that program, surface treatments were investigated for the improvement of boron filament-resin composite strength. The results showed the need for an oxide-free surface in order to achieve better filament-resin bonding. This work, combined with the requirements of uniform filament spacing in tapes and composites on other Air Force sponsored programs, led to the approach of applying a resin-sheath coating, up to about 0.5 mil thick, to the boron filament immediately after it emerges from the reactor. This was demonstrated with both boron on tungsten and on glass filaments using several epoxy and phenolic base resins in this program.

#### B. FEASIBILITY STUDIES

Adapting a resin coating chamber to the end of the reactor was shown to be feasible in preliminary in-line resin coating of boron filaments. These experiments were carried out with a setup shown schematically in Figure 60. The freshly formed filament was passed through a small hole into a vacuum chamber and then through another small hole into the nitrogen chamber and finally passed through a resin bath. After leaving the coater, the filament was passed through a staging chamber where the resin was "B" staged. The length of the staging chamber and its temperature depend upon the resin, the concentration of the resin in solution, the desired advancement, and the speed of the reactor. As an example, using a resin solution of 30

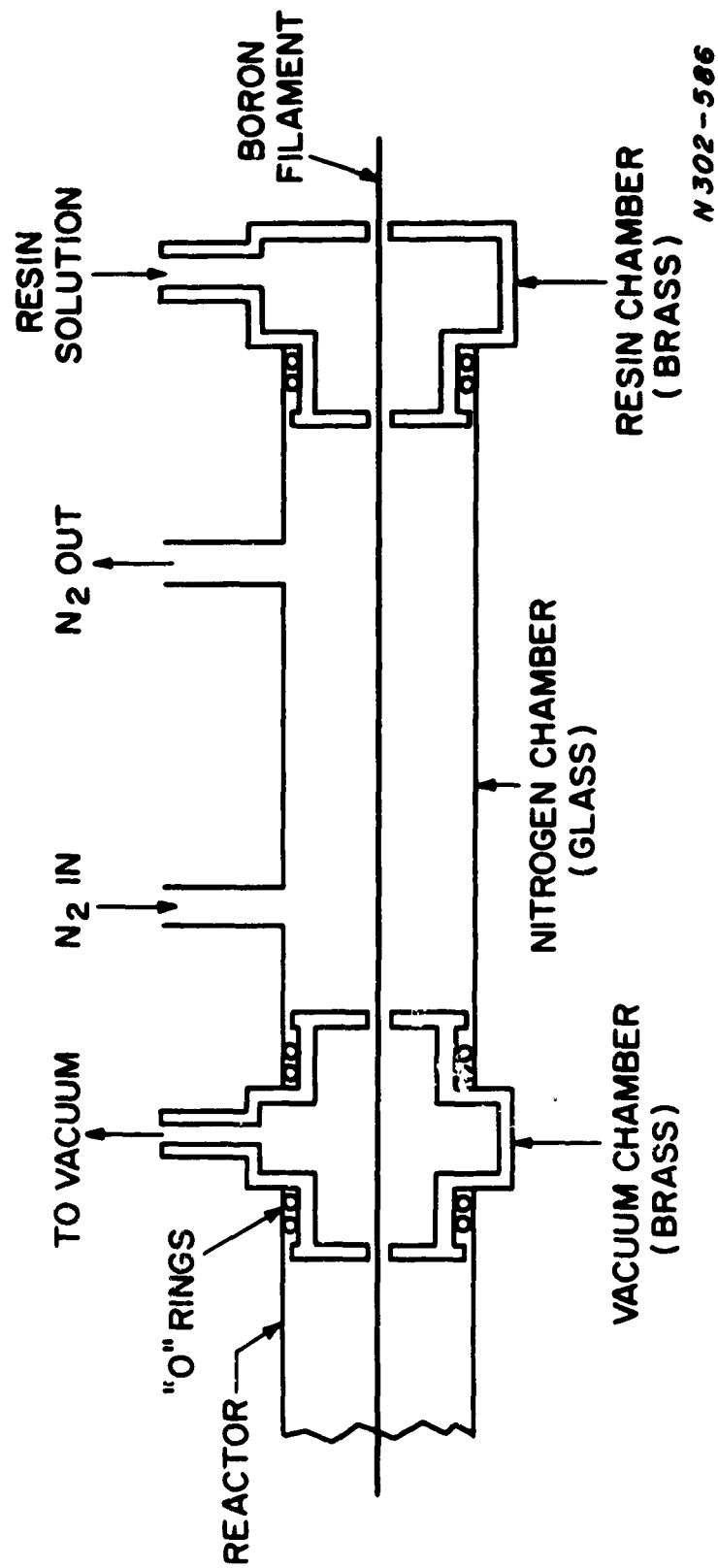


Figure 60. In Line Resin Coater

parts HT-424, 10 parts acetone and 1 part DMF, it was determined that a filament moving at 6 ft/min. was sufficiently advanced to be spooled without filaments sticking to one another in a 1 ft. oven heated to 325°C.

It was also shown that the resin coater and staging chamber could be attached either to a horizontal or vertical reactor. The small hole through which the resin-coated filament must pass to the tower serves also as a resin thickness gage for the sheath coating.

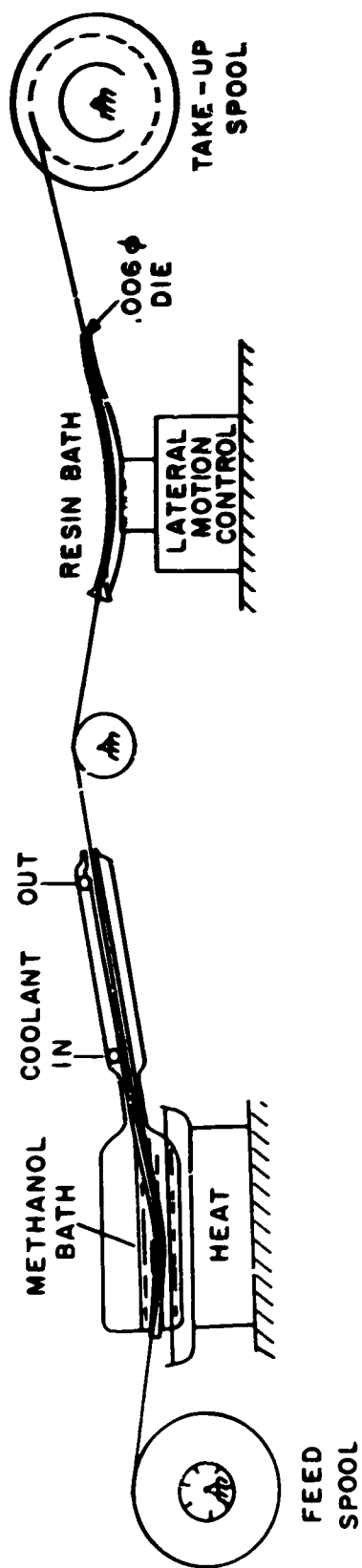
### C. RESIN COATING EVALUATIONS

In order to determine the proper coating parameters to use for various resin systems, preliminary studies were conducted on the effects of surface treatments, resin viscosity, degree-of-advancement, coating thickness, spacing and coating speeds. Coater length was not included in this evaluation since reactor design and speeds were not finalized. The coating apparatus used for this work is shown schematically in Figure 61. Boron/tungsten filaments produced from very early runs were used for coating, tape preparation, and composite preparation purposes. Also, boron produced by the hydride process was used in preparing tapes and composites described in the section on composite fabrication.

#### 1. Resin Systems

The basic resin systems used in this work were epoxies, based on epichlorohydrin-bisphenol "A" (Shell Epon 828), epoxy-novolac (Dow DEN 438), unmodified phenolics (Monsanto SC-1008), and modified phenolics (American Cyanamid HT-424 and General Electric VM-129).

The curing agents used with the conventional epoxies were m-phenylene diamine and Versamid 140. The epoxy-novolac was catalyzed with hexahydro-phthalic anhydride and Ciba's proprietary accelerator (DP-128) which had been developed for filament-winding applications. It is a tertiary amine salt which purportedly has many advantages over the more commonly used accelerators for anhydride curing of epoxies. It provides longer pot life. It lowers the initial viscosity of the particularly high viscosity novolac systems, and it is also known to have produced higher heat distortion temperatures with mild cures. Higher tensile elongation results with no loss



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Figure 61. Laboratory Setup for Treating and Resin Coating Boron Filaments

in tensile strength. Unreinforced castings, approximately 1/2" thick, of this formulation were prepared. The property data are as follows:

Cast Resin Properties of Epoxy-Novolac (DEN 438)

Formulation:

Resin: DEN 438 (100 PBW)  
Curing Agent: HHPA (90 PBW)  
Accelerator: DP-128 (2.0 PBW)  
Viscosity:  $19 \times 10^6$   
(base resin)  
@ 25°C, cps  
Viscosity:  $1-2 \times 10^3$  (within 1 hour)  
(formulation)  
@ 50°C, cps  
Viscosity:  $\sim 4 \times 10^3$  (after 16 hours)  
(formulation)  
@ 25°C, cps

Cure Schedule:

2 hrs. at 100°C (212°F)  
+2 hrs. at 149°C (300°F)  
+3 hrs. at 175°C (350°F)  
Slow cool-down to R.T.

Property Data

Sp. Gr.	1.22
Hardness, Barcol 934	42
Tensile Str. $\times 10^3$ psi	11.2 - 13.3
Elongation, % (at failure)	7 - 9.6

Barcol hardness was measured before and after post-cure and no change occurred, indicating a well-cured casting.

HT-424 is a two part (A&B) epoxy-modified phenolic adhesive system which proved to perform very well as the matrix for filament wound boron (B/W) re-entry structures.

The amine-modified phenolic system (VM-129) was prepared in the Space Sciences Laboratory under another program<sup>(12)</sup>. A patent application has been opened for this system, since improvement is noted in tape preparation and interlaminar shear strength is increased by ~100% over unmodified phenolics used. Further improvement of amine modified phenolic

composites properties was noted with methanol treatment of the boron surface.

## 2. Surface Treatments

Since in this evaluation aged and exposed boron on tungsten was used, it was decided that it was important to assess the effects of surface treatment as opposed to no treatment on the wetting characteristics of the boron filament.

Although not completely due to the untreated boron surface, the properties shown in Table XXII indicate the value of removing the oxide layer prior to resin coating. The data show an increase in flexural stress of approximately 100% simply by using an amine-modified phenolic on an untreated boron surface. This improvement is probably due to the fact that increased nitrogen content in the resin system makes it substantive to a material such as boron. A noted improvement is made both in flexural stress and shear strength when the boron surface is treated with a methanol-amine solution immediately followed by a coating of amine-modified phenolic.

It is reasonably safe to assume that coating an untreated boron surface contributes to poor interface bonding with most resin systems. Other factors contributing to poor results may be coating speed, viscosity of the resin, and temperature. An example of poor resin coating of untreated boron filaments is shown in Figure 62. When a tape is formed from this kind of coated filament, poor spacing results, heavy resin deposits exist, and pock marks develop on the tape surface which result from volatile release and poor flow upon softening in the "B" staging process.

First attempts were to run a sufficient length of filament through the laboratory set-up shown in Figure 61 and, as the alcohol treated and resin coated filament emerged from the .006" diameter die, it was immediately cured with infrared lamps prior to spooling. Visual examination of the coated filament showed variations in cured resin indicating hot spots. Micrometer readings of the resin cured areas indicated coatings up to .0025" on the diameter. The test pointed out the need for a better staging source.

**TABLE XXII**  
**FLEXURAL TESTS ON AMINE-MODIFIED PHENOLIC-BORON**  
**UNIDIRECTIONAL COMPOSITES**

<u>Spec. No.</u>	<u>Size</u>	<u>Mat'l Designation</u>	<u><math>\sigma</math>, Flex. Stress, psi, not ult.</u>	<u>Flex. Mod., E (by trans. deflec.) 10<sup>6</sup> psi</u>	<u><math>\sigma</math>, Shear, psi Failure Mode</u>	<u>16:1 Ratio Span Length</u>
1-59	0.127" x 0.134"	Untreated boron filament and phenolic resin	> 63,000	23.6	1853	2.0"
2-59	0.126" x 0.137"	(same as above)	> 60,000	24.4	1739	2.0"
3-59	0.113" x 0.127"	(same as above)	> 64,000	28.8	1684	2.0"
16-49	0.126" x 0.134"	Untreated boron filament and amine cured phenolic (VM-129)	> 121,500	26.5	3626	2.0"
17-49	0.122" x 0.129"	(same as above)	> 123,150	27.2	3720	2.0"
						<u>12:1 Ratio</u>
1-62A	.059" x .112"	Untreated boron filament and phenolic resin	> 37,600	7.7	1387	0.70"
1-62B	.048" x .112"	(same as above)	> 44,000	12.1	1500	0.60"
10-59	.064" x .129"	Amine treated boron filament and amine cured phenolic	> 168,300	17.2	6000	0.85"
10-59A	.063" x .131"	(same as above)	> 170,850	22.5	6090	0.85"
11-59	.073" x .116"	(same as above)	> 144,500	16.2	6000	0.85"

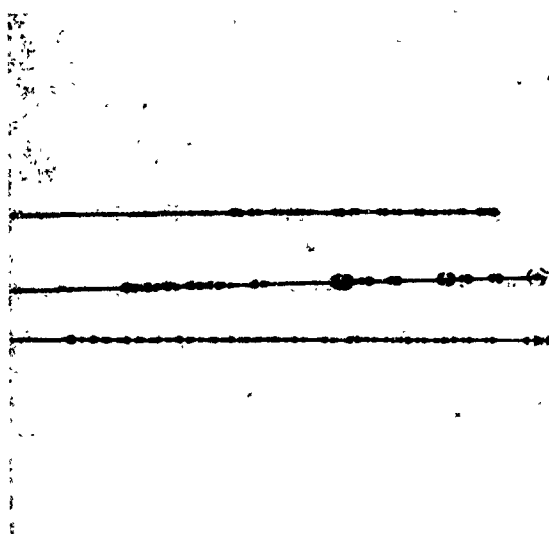


Figure 62. Poor Resin Wetting of Untreated Boron Surfaces



#### D. TAPE PREPARATION

Work was extended to some tape preparation to determine filament spacing limitations and possible extension of in-line resin coating to tape manufacture.

The laboratory set-up was slightly modified to adequately prepare boron tapes. The modification consisted in extending the distance between the .006" diameter die and take-up spool. A hot plate with a tube 12" long and 1/2" in diameter in good thermal contact with the heating surface was placed in this location. This served as a staging chamber for the surface coating. The chamber temperature was maintained at approximately 275°F. This set-up proved more satisfactory than only infrared lamps, but probably not as well as if a much longer chamber were used. The combination of the 12" tube and infrared lamps was later found to be adequate for our evaluation.

The process used in ensuing evaluations was that of passing a single filament through a hot methanol bath (80°C), allowing a small amount of time (~10 seconds) exposure to the atmosphere for solvent evaporation, followed by passage into the resin bath, emerging through a .006" diameter die for uniform resin coating, through the initial staging chamber, and finally spooling the tape on a mylar substrate (.0015" thick). When the desired tape width was obtained, the filament was cut off and further "B" staging was accomplished by using infrared lamps set at a fixed distance from the tape, while rotating the spool. The distance from lamp to the tape surface varied with the type of resin used, but in any case was never more than 10".

The feed and take-up spools were fixed in place. During the process of feeding and spool-up, filament breakage was initially high; however, the incorporation of the lateral motion control helped this situation and served two functions. First, it allowed for uniform release of boron from the feed spool and, secondly, it facilitated the preparation of tapes with uniform filament spacing. Single layer tapes up to 1.5" wide x 20" long are possible on this equipment.

Filament speeds varied with the resin system used. One of the dominating factors in determining the speed to use is resin viscosity. It

was determined that with a highly tacky system such as HT-424, possessing a viscosity @ 25°C of 1500 cps, the faster speeds produced a heavier coating on the filament, and at speeds around 4 to 6 ft/min., the coating was uniform. Achieving varying viscosities is possible by altering the amounts of parts A and B of the primer system with HT-424 primer thinner. Cutting the system with acetone (10% by weight) and dimethyl formamide (1% by weight) worked well in this particular set-up.

Where the epoxies, phenolics and amine-modified phenolics are concerned, speeds of 6 to 8 ft/min. were found suitable. Although the viscosities of each of these systems varied from  $2 \times 10^3$  cps at 25°C, coating was not as difficult since these resins were not as tacky as the HT-424 adhesive system.

The degree to which a resin is advanced in tape preparation is of prime importance as far as ultimate composite strength is concerned. If a resin is too advanced-to almost the "C" stage (which is the final, infusible state) - interlaminar flow during cure is reduced; hence, physical and mechanical properties are greatly affected. For example, composites prepared from tapes made of more advanced HT-424 resin (~90%) produced flexure stress values  $> 81 \times 10^3$  psi and shear strength values of  $3.1 \times 10^3$  psi, whereas composites with HT-424 resin less advanced (~60%) resulted in flexural stress values of  $> 128 \times 10^3$  psi and shear strength values of  $4.9 \times 10^3$  psi.

Although feasibility was shown in coating boron filaments with various types of resins, epoxies produce better wetting and coating uniformity. Microscopic studies of tapes prepared on another program<sup>(12)</sup> with epoxy resin have shown highly satisfactory filament coating and uniform spacing. A magnified area of tape having 0.00073" spacing is shown in Figure 63.

Through the incorporation of an amine modifier in a phenolic resin, wettability and coating were improved as well as composite properties. Figure 64 shows a 1-1/4" wide amine-modified phenolic-boron tape on a spool. A cross section of this tape showing fiber spacing at 16X magnification is shown in Figure 65. In this instance, also, tapes were highly advanced

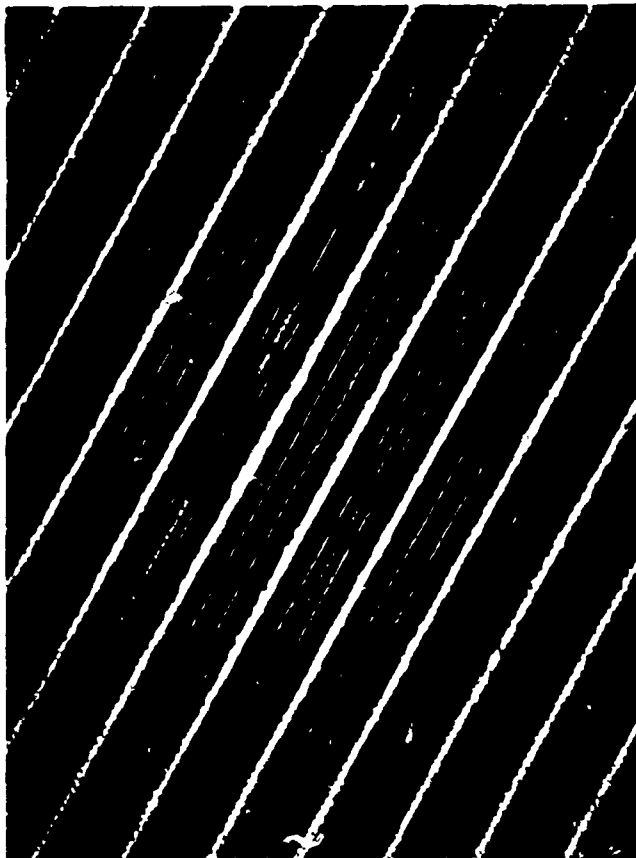


Figure 63. A Magnified Section of Boron/Resin Tape Showing Uniform Figuer Spacing. Mag. 99X



Figure 64. Amine-Modified Phenolic/Boron Tape 1-1/4" Wide

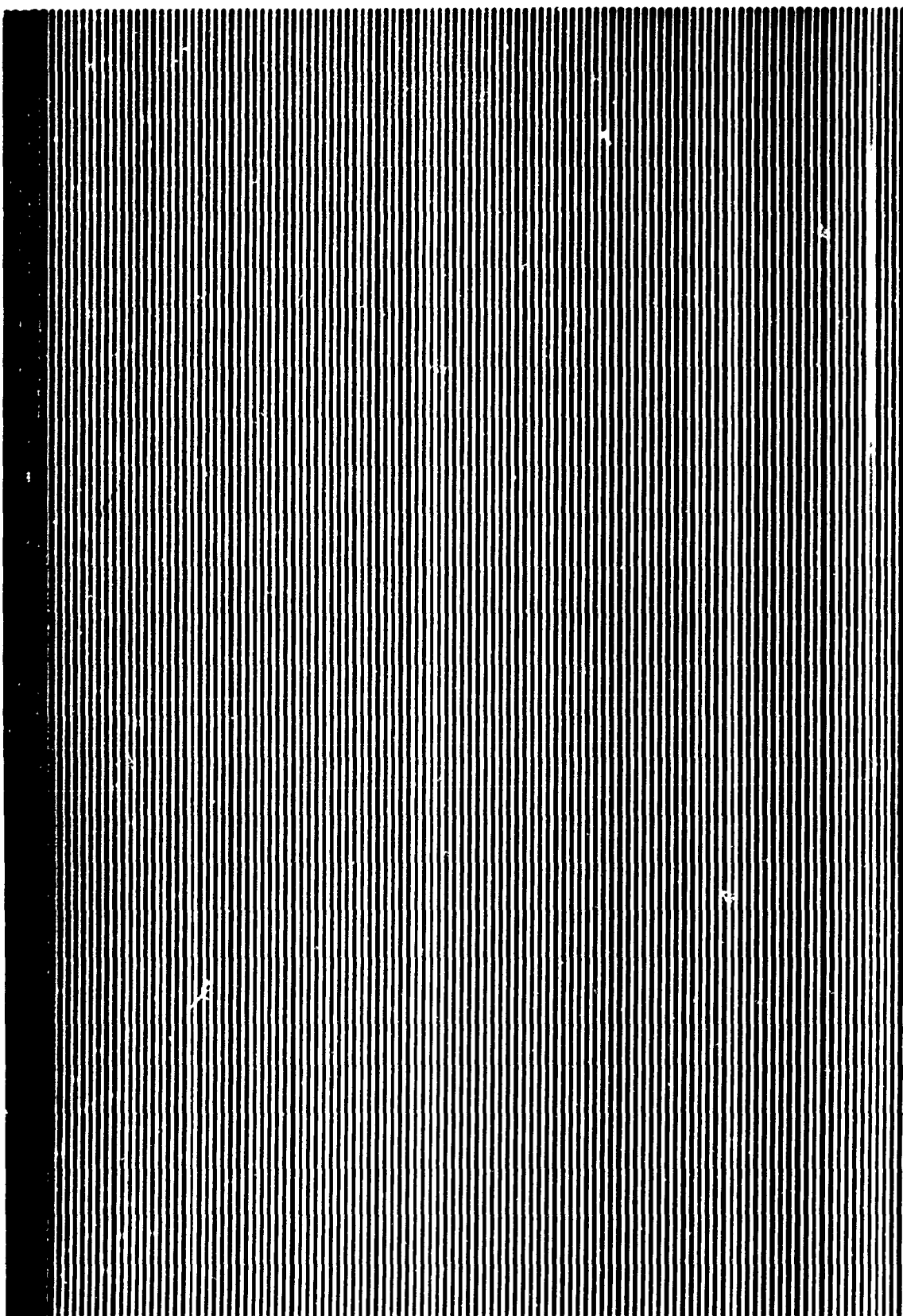


Figure 65. Amine-Modified Phenolic Boron Tape 1" Cross Section Showing Fiber Spacing (16X).

as well as only slightly advanced for composite fabrication.

#### E. COMPOSITE FABRICATION

Unidirectional composites  $\sim 1/8 \times 4.5$ " long were prepared with some of the resins evaluated in this program, namely, amine-modified phenolic, epoxy-novolac (DEN 438), and HT-424. Those made with HT-424 are briefly described in the section under tape preparation. Others were made by 3M and are also described.

##### 1. Epoxy-Novolac/Boron Composites

As mentioned earlier, epoxy-novolac/boron composites were prepared with boron filaments produced by both the hydride and halide processes. Small sections of tape  $\sim 1/8$ " wide  $\times 6.5$ " long were cut from larger tapes and placed in several layers in side loading molds. The bar mold used in curing composites is shown in Figure 66. The loaded mold was then placed in a press with  $\sim 30$  psi pressure and platten temperature of  $\sim 230^{\circ}$ - $240^{\circ}$ F. The mold temperature was approximately  $210$ - $220^{\circ}$ F. This temperature was held for 2 hrs., after which the mold temperature was increased to  $300^{\circ}$ - $310^{\circ}$ F and held for 2 hrs. Post-cure followed immediately for 3 hrs. at  $350^{\circ}$  to  $360^{\circ}$ F. During the cure cycle, four composites were cure simultaneously in separate molds. Resin flow was observed at mold ends but the filaments remained intact. After curing, the composites were cooled down to room temperature under the specified pressure. The molds were stripped and the finished specimen dimensions determined, before the specimens were tested in 3-point bending in an Instron machine using a span ratio of 12:1.

##### 2. Amine-Modified Phenolic/Boron Composites

Boron filaments used in these composites were produced by the halide process. Fabricating techniques were the same as with epoxy-novolac except for the cure schedule. These composites were cured for 2 hrs. at  $200^{\circ}$ - $210^{\circ}$ F at  $\sim 25$  psi on composites, followed by 2 hrs. at  $240^{\circ}$ - $250^{\circ}$ F, then for 16 hrs. at  $275^{\circ}$ - $290^{\circ}$ , and finally they were post-cured for 2 hrs. at  $310^{\circ}$ - $315^{\circ}$ F under pressure.

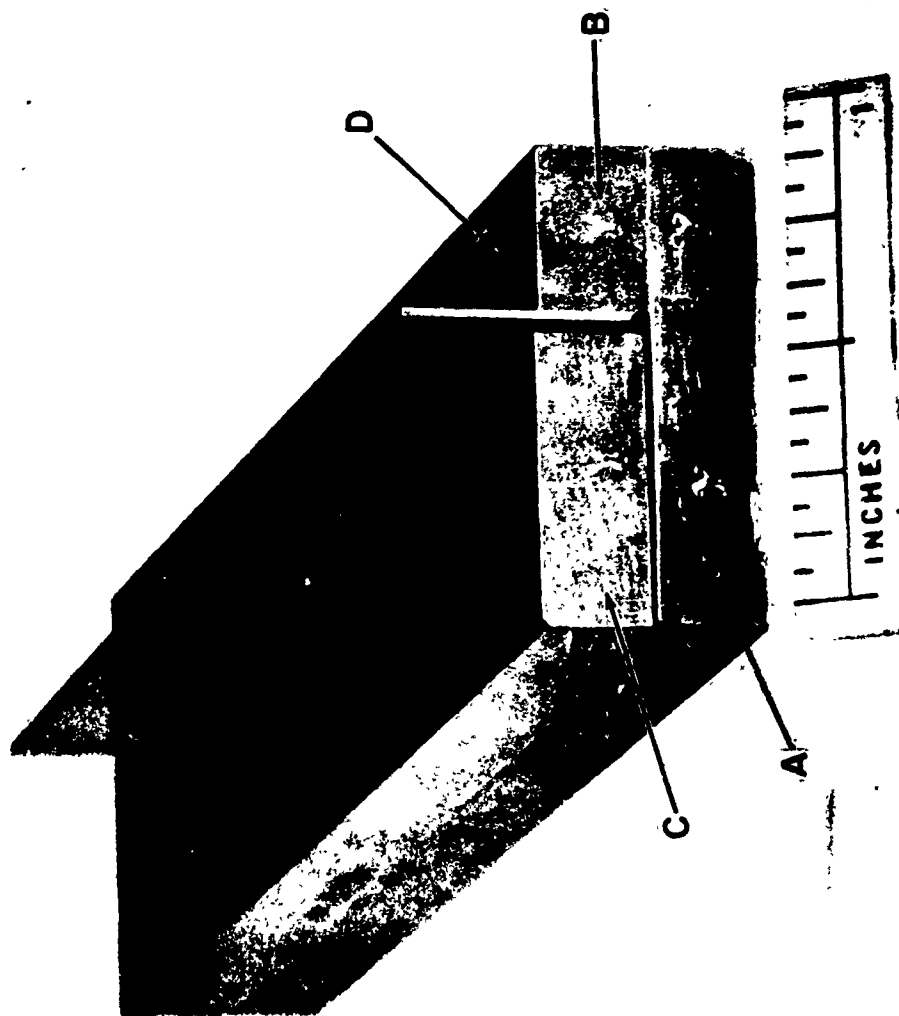


Figure 66. Mold Used in the Preparation of Bar Specimens of Boron Reinforced Resin Composites.

## F. TEST RESULTS

### 1. Epoxy-Novolac/Boron Composites

The data obtained from flexural and shear tests are presented in Table XXIII. All specimens were tested at 0.02 in/min. The first four specimens shown failed in shear, whereas four of the six boron-hydride epoxy specimens failed in flexure and the other two of the six failed in shear. It should be realized that the flexural tests are for comparative purposes and the values noted are not to be taken as ultimate, because during bending there was a certain amount of shear interaction.

On the basis of rule of mixtures, the bend strength to density ratio for the hydride boron on glass filaments composites is slightly higher than the comparable test results for the halide boron on tungsten filaments. This is in contrast to the tensile strength to density of the individual filaments which were used in these experiments. In the filament tensile tests, the boron on tungsten showed a slightly higher strength to weight ratio.

### 2. Amine-Modified Phenolic/Boron Composites

These composites were prepared with highly advanced resin, highly tacky resin and the combination of these two extreme conditions in alternate layer layup. Specimens were likewise tested in 3-point bending in an Instron tester with a crosshead speed of 0.02"/min. The data for flexure stress and shear strength are presented in Table XXIV. In all of these specimens, the failure mode was shear as there was no evidence of fiber fracture during bending. Interlaminar separation was observed during the tests. Flexure values are, therefore, not ultimate.

It is important to note the low shear values for the highly advanced and combined resin conditions as compared with almost a 100% improvement for those composites prepared with the high tack material. This data was presented in order to demonstrate the importance of resin advancement in tape and composite fabrication. It is believed that material possessing a slightly higher degree of resin advancement (~25-30%) would produce composites with better properties because of proper flow during cure and

TABLE XXIII

**FLEXURAL TESTS ON EPOXY-NOVOLAC/BORON UNIDIRECTIONAL COMPOSITES**  
**(3-Point Bending--12:1 Ratio)**

Material Designation	Spec. No.	W, in.	T, in.	E (by transverse deflection) $10^6$ psi	$\tau$ , Shear, psi	$\sigma$ , Flex. Str., psi	P, lbs.	Composite Density, g/in. <sup>3</sup>	V/in	$S_c/10^6$ in.)	Remarks
Epoxy-novolac resin & boron (halide), Boron MeOH treated prior to resin coating.	69-1AA	0.141	0.112	20.44	8,200	-206,300	172	0.0810	72.10	2.54	Failure made in shear flex, not ultimate.
Epoxy-novolac resin & boron (halide), Boron MeOH treated prior to resin coating.	69-1AB	0.143	0.112	15.12	5,700	-150,500	122	0.0810	72.00	1.86	Failure made in shear flex, not ultimate.
Epoxy-novolac resin & boron (halide), Boron MeOH treated prior to resin coating.	69-2AA	0.145	0.110	26.01	8,350	-210,000	175	0.0833	71.80	2.52	Failure made in shear flex, not ultimate.
Epoxy-novolac resin & boron (halide), Boron MeOH treated prior to resin coating.	69-2AB	0.143	0.112	18.80	8,470	-216,200	155	0.0833	71.60	2.60	Failure made in shear flex, not ultimate.
Epoxy-novolac resin & boron (hydride), Boron MeOH treated prior to resin coating.	69-5A1A	0.112	0.091	12.85	-6,500	207,800	89	0.0752	63.40	2.76	Failure made in shear flex, not ultimate.
Epoxy-novolac resin & boron (hydride), Boron MeOH treated prior to resin coating.	69-5A1B	0.110	0.093	12.46	-5,925	178,950	81	0.0752	63.24	2.38	Failure made in shear flex, not ultimate.
Epoxy-novolac resin & boron (hydride), Boron MeOH treated prior to resin coating.	69-6A1A	0.110	0.093	13.41	5,650	-170,200	77	0.0748	63.10	2.27	Failure made in shear flex, not ultimate.
Epoxy-novolac resin & boron (hydride), Boron MeOH treated prior to resin coating.	69-6A1B	0.110	0.093	13.40	6,010	-181,270	82	0.0748	63.30	2.42	Failure made in shear flex, not ultimate.
Epoxy-novolac resin & boron (hydride), Boron MeOH treated prior to resin coating.	69-7A1A	0.111	0.102	27.90	-5,300	166,000	79	0.0754	74.60	2.90	Failure made in shear flex, not ultimate.
Epoxy-novolac resin & boron (hydride), Boron MeOH treated prior to resin coating.	69-7A1B	0.112	0.097	13.10	-5,600	172,200	82	0.0755	76.60	2.28	Failure made in shear flex, not ultimate.



TABLE XXIV

FLEXURAL TESTS ON AMINE-MODIFIED PHENOLIC-BORON UNIDIRECTIONAL COMPOSITES  
(3-Point Bending--12:1 Ratio Span)

<u>Spec. No.</u>	<u>W, in.</u>	<u>T, in.</u>	<u>Span L.</u>	<u>E (by trans. defl.) 10<sup>6</sup> psi</u>	<u>T, Shear, psi Failure Mode</u>	<u><math>\sigma</math>, Flex Stress, psi, (not ult.)</u>	<u>P, max, lbs.</u>	<u>Material Designations</u>
68-AP-1A	0.118	0.065	0.75	2.1	2,610	> 63,000	27	amine-cured phenolic/boron; resin advanced
68-AP-1B	0.117	0.067	0.75	0.72	2,660	> 64,100	27.5	~ 85-90%; 14 layers used.
68-AP-2A	0.113	0.077	0.80	1.2	1,225	> 65,500	35.5	amine-cured phenolic/boron; 14 layers used;
68-AP-2B	0.113	0.077	0.80	1.21	2,450	> 51,700	28	7 layers advanced resin, 7 layers tacky resin.
68-AP-3A	0.116	0.063	0.70	15.7	4,140	> 140,000	40	amine-cured phenolic/boron; resin ~ 10% advanced on tape.
68-AP-3B	0.115	0.064	0.70	13.3	4,400	> 102,650	44	(same as 3A)
68-AP-4A	0.112	0.066	0.75	13.8	4,580	> 113,760	45	(same as 3A)
68-AP-4B	0.113	0.066	0.75	18.5	4,230	> 106,200	42	(same as 3A)

more uniform resin distribution in the finished material. The improvement would be derived from the narrower viscosity range that the resin would experience during the cure cycle. The specimens made with the combined materials demonstrates clearly that poor properties can result from combining two materials with dissimilar properties while curing with a common cure cycle.

### 3. 3M Boron/Epoxy Composites

A small sample (about 2000 ft) of boron on glass (silica) filaments were supplied to 3M for preliminary trials with this type of filament. The data from these test specimens is shown in Table XXV with two sets of boron on tungsten filament reinforced composites for comparison. Although the glass core filament in these tests did not handle as well as the tungsten core material (probably due to weak spots at nodules) the composite properties indicate good conversion of filament properties into composite properties.

TABLE XXV

#### 3M RESULTS ON PRELIMINARY SAMPLES OF BORON ON GLASS

	Boron-on-Glass	Boron/W	Boron/W
Filament Tensile Strength (PSI)	300,000	450,000*	400,000*
Filament Specific Gravity (G/CC)	2.28	2.62	2.62
Composite Specific Gravity (G/CC) at 30 W/O Resin - 70 W/O Filament	1.81	2.05	2.05
Flexural Strength (PSI)	195,000	250,000	192,000
Beam Shear Strength	12,450	16,000	14,600

\*Estimated

## SECTION VII

### TASK V - AUTOMATIC CONTROLS

Objective: To identify the principle parameters in the overall process which could be used to achieve automatic process and product control; to define control variables, and to recommend methods and equipment.

#### A. BACKGROUND

In order to produce a material at minimum cost it is important to reduce the cost of labor as well as that of the raw materials. In many instances, the former constitutes the bulk of the delivered price to the consumer or fabricator. Automatic monitoring and control of a wide range of chemical and mechanical operations has permitted significant cost reductions to be achieved in many instances with consequent increased market potential as prices decreased. However, the application of these principals depends upon a knowledge of the process and the key steps, the control and regulation of which must be automatically accomplished to insure routine production of specification material.

In a simple case, a measurable property of the product, the value of which is determined by a single, controllable process parameter is automatically measured, and the signal resulting from the measurement is used to vary the control parameter in order to maintain the desired value of the property. If, for example, in drawing a glass monofilament at a given constant speed, the diameter can be measured automatically, the output of the measurement can be used to control the orifice or bushing temperature so that a constant diameter result will always be obtained. A more complex process might be able to be broken down into a series of simpler elements, each of which can be controlled automatically, or its complexities may be the result of interaction of more than one process parameter. The latter situation is somewhat more difficult to handle inasmuch as a rather complete knowledge of the internal mechanisms governing the degree of interaction is required to establish automatic control. In many cases, simple monitoring

of the parameters is undertaken at the outset, with manual adjustments made as required on the several interlocking variables.

#### B. APPLICATION TO INTEGRATED PROCESS

The integrated boron filament process, from the substrate drawing step through the resin coating of the finished boron filament, consists, as far as automation possibilities are concerned, of a series of steps of varying degrees of complexity. These consist of: (1) drawing the substrate to a specified diameter, (2) applying a conductive coating of uniform resistance, (3) depositing boron to give a filament of specified strength, modulus density, and diameter, and (4) coating the boron filament with a resin. Each of these consecutive steps must yield a product which meets the needs of the subsequent step in order to produce the desired final product. The latter is described principally by the following specifications:

Tensile Strength	400,000 psi min. avg.
Diameter	4 mils $\pm$ 0.1
Modulus	$52 \times 10^6$ psi
Density	Less than 2.35 gm/cm <sup>3</sup>

The overall design philosophy of the high-speed reaction system was to have as few manually set or varied controls as possible. Fixed orifice flow meters for example would be used in place of the conventional float type. Other process parameters were expected to be independently controlled or preset, as for example, filament draw speed. Ideally, one would prefer to have as few control points as possible. By presetting or predetermining optimum conditions this could be accomplished.

In considering automatic control, it is important to distinguish between in-line product monitoring and conventional quality control. In the latter case it is customary to set aside a representative sample of a given production unit for routine determination of key properties. In the present case, where a continuous filament is the product, it is of little value in reducing costs since it is an ex post facto approach to control. In-line controls must be relied upon to prevent wasteful production of substandard material and an excessive

number of splices as a result of sampling since both represent costly distractions of labor. To appreciate the magnitude of this aspect, one need only consider the difficulty of sampling adequately the properties of 80,000 feet of filament which would represent the result of approximately 80 minutes of running time at maximum speed, and of returning test results to operating personnel in time to restore an out of balance situation in one of the sub-specifications.

In-line testing of product specifications means essentially non-destructive testing or measuring. In certain areas little difficulty was experienced in delineating the critical control point, a useful response and a method of using an output signal from the measurement to regulate the process. In other areas, development of appropriate equipment had not yet been accomplished and a need was seen for the adaptation of methods and equipment already in use in related fields (textiles and synthetic organic filaments for example) or for the development of new instrumentation.

The individual steps in the overall process were considered in the light of their primary parametric dependence, i.e., the variables which could be monitored and possibly controlled most readily. It was not the initial intent to attempt the setting up of servo or feedback loops to achieve actual process control of an operational basis, nor was quality control in the customary sense a matter for consideration.

#### 1. Step 1 - Glass Drawing

As was discussed in Task 1, the drawing of glass substrate from the melt was carried out by heating the glass to an appropriate temperature in a high temperature crucible, and drawing it through a heated bushing. The principal control property of the substrate would be its diameter since the vapor deposition of boron closely reproduces deviations in substrate diameter. Given a constant operating or drawing speed, control of bushing temperature should establish control over diameter and vice versa. A secondary requirement in the glass drawing was to maintain a sufficient head of molten glass over the drawing point, or to maintain a proper rate of addition of new glass to the melt without upsetting temperature conditions within the melt.

This latter problem can be solved with a mechanical feed mechanism to advance glass canes at the proper rate.

Control of diameters to within 10% at the one mil diameter level was a problem which was receiving the attention of the GE Lamp Dept. research staff at the time. The GE Wire Gauge, developed for determining the diameter of tungsten wire above about 2.2 mils, had not been found to be sufficiently precise in the diameter range below this point. However, a second device of a proprietary nature based on a diffraction principle was undergoing development, and was expected to be available to this program when needed. Observations were made of its performance in measuring the diameter of samples of the substrate to be produced in this process. It was found to be sensitive to diameter variations within the range of interest and was recommended for this purpose. The output signal from the photoelectric detector of this device would also be suitable for operating a controller for the bushing heating circuit to enable temperature adjustments to be made automatically which would return the bushing temperature to the specified point without overshooting. This control could be set to work from above or below the temperature required to draw 1-mil glass.

In practice, operation of the drawing furnace was found to be quite stable with little adjustment of temperature being required manually due to the closely following response of the SCR controlled power supply. Further inquiries on this task therefore were not carried out.

## 2. Step 2. - Conductive Coating

As has been stated in Task II, the requirements for a satisfactory conductive coating included uniformity of resistance, continuity, and stability to the deposition process. Subsequent studies with filament drawn and coated both with carbon from suspension and pyrolytic carbon established that either coating conducted without difficulty in the deposition process once baking conditions had been established for the former process. However, resistance variation and continuity were problems with the more extensively studied of the two approaches, the coating from suspension. Both could be monitored with conventional resistance measuring devices up to a speed limit

which was not determined, since it would depend upon the response time of the particular meters chosen. If resistance were to be measured for example on a 1-foot standard length, the time spent for noting a variation would be one millisecond at 1000 feet per minute. Furthermore, the resistance measurement would be the average resistance per foot. More rapid response techniques, such as the use of fast sweep oscilloscopes would give more closely spaced readings which could be recorded on a high speed recorder (e.g. Varian Visicorder). The value of this procedure would be doubtful, however, since no adequate feedback circuit could be designed to control the coating procedure. The latter it will be recalled consisted basically of a series of rollers which wiped the filament with a thin layer of a commercial graphite dispersion. Control of the coating thickness, resistance and variation must be made, therefore, by establishing the critical aspects of the coating technique and controlling them. Such parameters as dispersion thickness, pH, roller speed, drying temperature, etc. figure in this. Since the key variables and critical values were not identified, no recommendation could be made regarding automatic control at this point. However, it could be pointed out that inasmuch as the coatings applied from graphite suspensions usually had a finite thickness within the detectable range of the substrate diameter measuring device referred to above, this instrument could be used effectively to monitor diameter, although control might not be feasible at the present time.

The pyrolytic coating method was not fully explored. However, again resistance, variation, and continuity are critical for satisfactory coatings. The same problems in measuring resistance variation and in applying readout signals for controlling the coating process are applicable here. In view of preliminary experiments made with this process (Task II), the variation in resistance would be expected to be minimal if substrate diameter were adequately controlled by drawing from the melt. Equilibrium coating conditions in gas phase coating, once established, should be maintained since they depend primarily on the maintenance of a steady temperature in the preheater furnace and on steady gas flow of uniform composition. Barring line plugs in

flow meters and failure to maintain constant backpressures, these operations are not normally difficult to control. Since the pyrolysis is a molecular process, based on an inexpensive source, thickness does not enter the picture in a serious way (unless cost becomes a consideration as in the case of tungsten coatings from tungsten hexacarbonyl decomposition). In an equilibrium mode of operation, with good temperature control, the resistance of the substrate should depend on the diameter of the incoming glass filament; the principal source of variation in the coating step would be expected to arise through variations in the preheater oven temperature - this device could be placed on a standard temperature controller with a minimum deviation such as is discussed for control the the drawing temperature in Task I.

### 3. Step 3 - Boron Deposition

The deposition of boron is undoubtedly the most complex step in the overall process. Past experience has shown that in an equilibrium operating mode for any given set of conditions, diameter and modulus are not subject to sudden unexplained variation. However, as was discussed in Task IV, tensile strength variations were troublesome when mercury contacts were used to conduct power to the substrate. Inasmuch as these would be dispensed with in a RF heated high speed reactor, consideration was then given to the reactor design and its performance with respect to the specifications of diameter, strength, modulus, and density. Only the first two were considered in the light of past experience with modulus and density performance.

A Hastings Denier Gauge was used to monitor the diameter of filament produced in the RF prototype reactor. Since only one power control was used to establish temperatures in all stages, the relationship between power input and diameter was quite direct. It was found possible to produce filament of any given diameter by adjusting the power setting until the Hastings Gauge gave the desired reading. Conversely, by using the gauge during start-up, it was possible to tune the filament in by means of its final diameter, at standard flow and pressure, rather than by observing the radiance level. In operating on a continuous basis with automatic power control facilities, the output of the gauge could be used to make minor power adjustments so as to



produce only 4 mil filament. This means that the variations which might exist in the substrate would also be compensated for, at least as far as total diameter is concerned. Since strong filament of nearly all diameters has been produced there is reason to expect that a minor adjustment in temperature which would increase or decrease the boron coating thickness by a small percentage of the total thickness, would not affect the filament strength.

With respect to tensile strength, it was found during investigation in Task IV that the principal sources of sub-specification filament were the mercury electrodes. With their elimination, i.e., using the RF heated reactor, filament strength was much more uniform with respect to average strength. Deviations from these averages were observed, but their causes were not pinpointed. In-line determination of tensile strength at the present time would have to be based on a capstan type of proof-test arrangement, set at some minimum value below which it would be uneconomical to operate. If the filament strength fell below this value, it would of course break, necessitating a splice or retaping of the leading end of the filament to the wind-up spool. Use of a device such as this for controlling the process does not appear to be practical. An indirect approach would appear to be more satisfactory. For example, the composition of the feed gas is known to affect filament strength (Task IV). Excessive hydrogen or pentaborane could be responsible for low strength filament. Either could be determined by gas chromatography, and control of the feed gas composition established by means of a controlled reservoir temperature. In a continuous recycle operation, this control point might well be in the recycle stream in the form of a cryogenic trap or solvent scrubber, to remove excess quantities of borane intermediates. The control amount would have to be determined by experiment. A control system such as this, however, presumes a greater knowledge of the deposition process in the RF heated reactor than is presently available.

#### 4. Step 4 - Resin Coating

A final processing step consisted of coating the freshly formed boron filament with a resin to protect it from atmospheric contamination. This

step was found to be experimentally relatively simple, and was therefore not investigated further at the filament speeds used at the time. At very high speeds, problems might be expected to arise from carrying resin out of the reservoir by friction. The magnitude of the problem would have to be determined, as well as the effects of resin viscosity, pressure head on the resin coating attachment, etc. before a control point could be established. In all probability, the result of difficulties in the resin coating step would make themselves felt in diameter variations of a presently unknown magnitude and varying degrees of resin staging. Again, however, once optimum equilibrium conditions were established, deviations in diameter could be monitored and the output used to adjust the resin pressure head or temperature. Staging of the resin at uniform composition could be done independently by temperature control at a given speed. However, until further work is done at high speeds, no recommendation can be made regarding the most appropriate control point or suitable instrumentation.

##### 5. Summary

The foregoing comments and preliminary recommendations may be summed up in the following manner:

Operation	Control Point	Instrumentation
Glass Drawing	Bushing Temperature	SCR power supply - diffraction wire gauge, reading diameter
Conductive Coating	Preheating Furnace	Resistance meter, controlling preheater temp.
Boron Deposition diameter:	Filament Temperature	Hastings Denier Gauge, reading diameter
tensile strength	Gas Composition	Gas chromatograph on feed composition control point.

## SECTION VIII

### PROJECTED PRODUCTION EQUIPMENT AND COSTS

#### A. PRELIMINARY HIGH SPEED PROCESS EQUIPMENT DESIGN

Considerable thought has been given to the general or conceptual design of a high speed reactor. Each of the tasks on which work was performed was derived from considering the overall system, both technically and economically. For example, the drawing of glass filaments is normally done at speeds of 10-30,000 ft. per minute, so the principal problem was to draw a monofilament of a suitable glass at speeds of a few hundred to a 1000 feet per minute. It was first judged that for economy of operation, from both the labor and capital investment standpoints, the boron filament deposition rate should be raised as much as possible. An order of magnitude over current practice is a challenging but achievable goal. In addition, a capability to draw and deposit on several filaments in each reactor was kept in mind but not extensively worked on; it now looks feasible by the use of RF heating.

Two general concepts of reactor design were considered. The first of these is shown in Figure 67. It has the advantage of being potentially more compact and therefore fitting the preliminary plant design discussed later. The second concept was based on an extrapolation of current designs and consisted of several tubes mounted parallel to each other with the whole array mounted either horizontally or vertically. This is shown in Figure 68. In this design the filament would pass through the first tube, turn 180° over a pulley, and go through the second tube, and so on. The total heated filament length in the reactor would be about 110 feet at the anticipated deposition rates and a filament draw speed of 1000 ft./min. Current deposition rates that yield good filament properties and efficient conversion of diborane suggest the need for a reactor 2-3 times this long. However, further process chemistry studies as discussed in Task IV offer some hope for achieving a shorter reactor length.

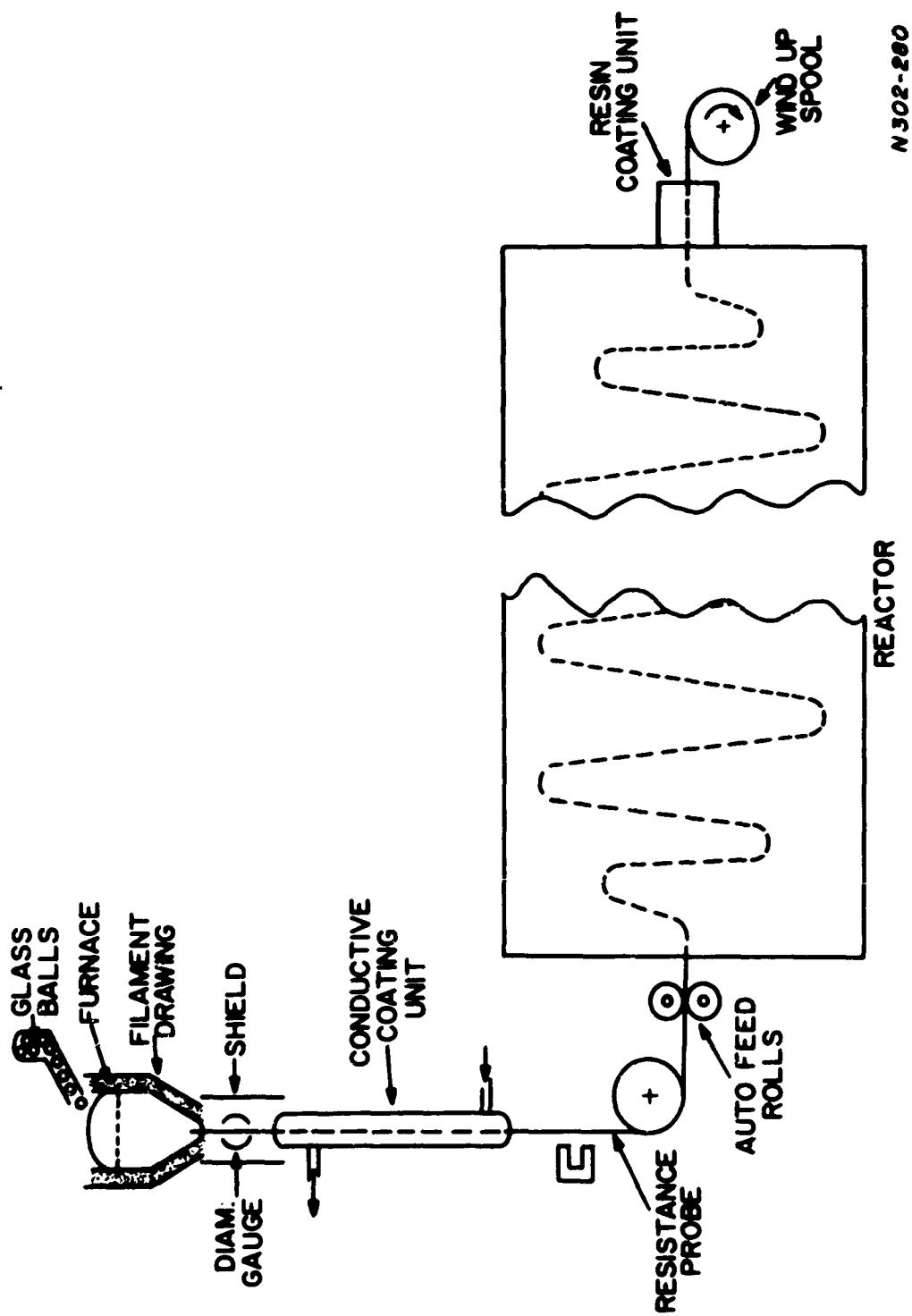
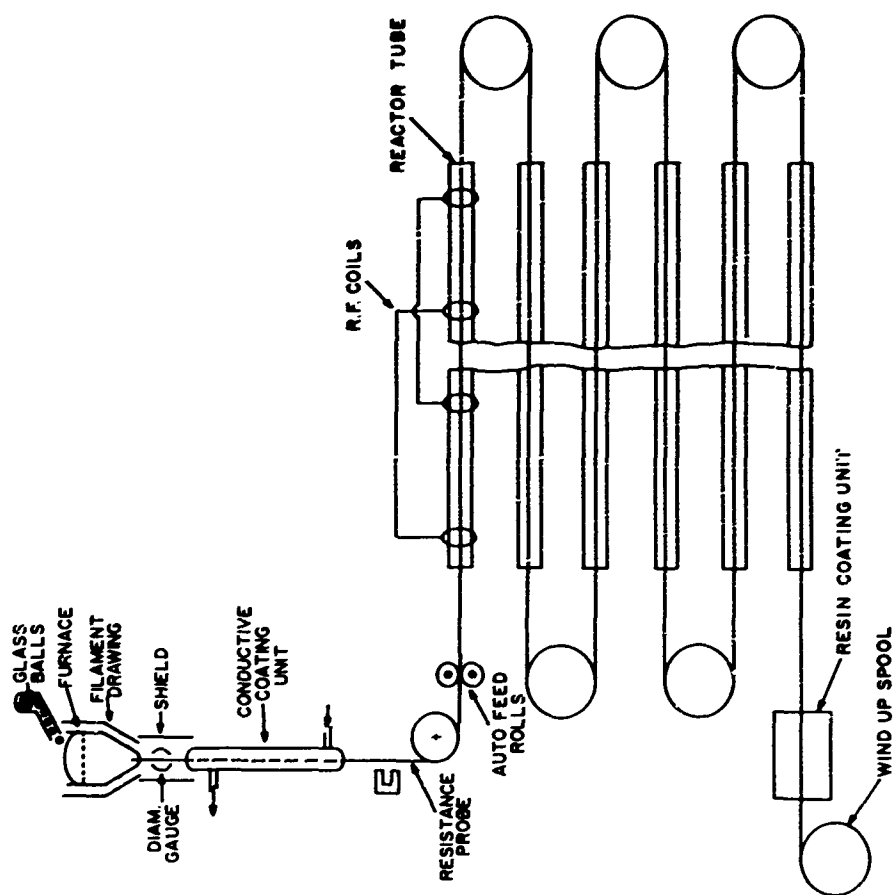


Figure 67. Conceptual Design for an Integrated Boron Filament Deposition Process.



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Figure 68. An Alternative Conceptual Design for an Integrated Boron Filament Process.

A major requirement of a high speed reactor is a method for rapid and simple threading so as to minimize non-productive down time and labor costs. It is believed that much of the equipment and technology for doing this is available for use or adaptation from the textile industry. In the case of the second type of reactor discussed above, a chain or belt having a threading eye attached at one or more points was envisioned to carry a leader through the reactor and out to the take-up reel where an operator would attach it. In the first or more compact reactor design shown in Figure 67 threading would be accomplished by lowering the upper set of pulleys between and below the lower set while an arm or telescoping tube would take a leader through the reactor between the sets of pulleys. Returning the upper pulleys to their initial position would put the filament into the zig-zag pattern indicated by the dotted lines in Figure 67.

Deposition reactors would be located along the dotted lines between the pulleys to direct the feed gas to the filament and minimize deposition onto pulleys or other auxiliary equipment.

#### B. PRELIMINARY PILOT PLANT DESIGN

Prior to the initiation of this program, a company funded study was made with the help of Catalytic Construction Company to arrive at a preliminary pilot plant design. A nominal gross capacity of about 30,000 lbs. per year with growth to 60,000 lbs./yr. was planned. The estimated cost of a complete new facility was \$6.8 million, including a 20% contingency, and a 10% architect-engineers fee.

The plant (see Figure 69) was designed around eight modular reactor units, each containing 15 vertical mercury contact reactors enclosed in a hood so that nitrogen could be used to provide a protective atmosphere. Operation would involve threading and readying the entire bank for operation, rolling it into a cubicle, plugging in gas and power supplies, running it remotely until it either needed to be shut down for cleaning or was down to too few filaments being processed due to breakage. At that point, it would be removed for cleaning and rethreading, while a spare unit was installed

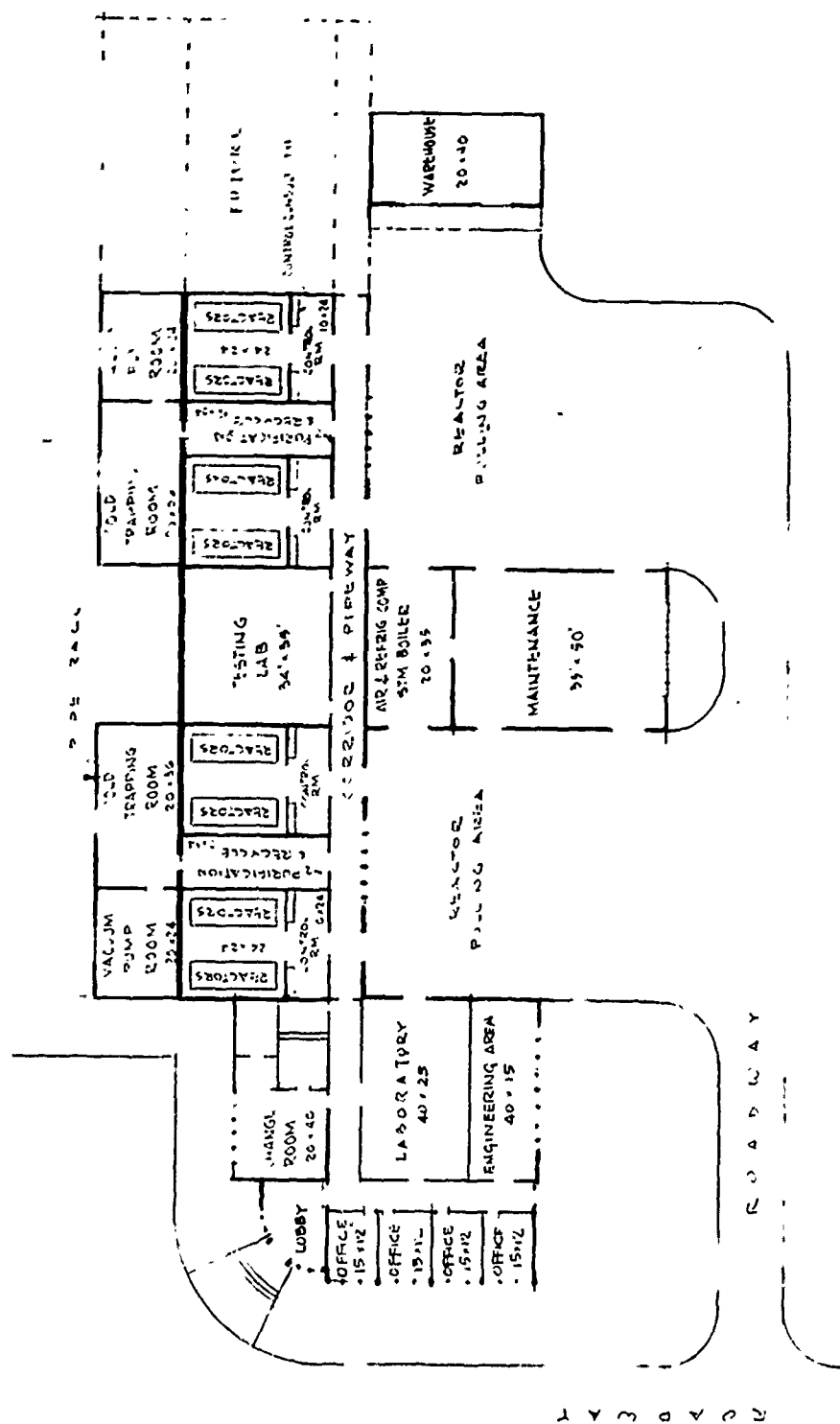


Figure 69. Plan View of Plant.

and used for production. Assuming 24-hour days and five-day weeks with filament being processed at 50 feet per minute, the 120 reactor plant could produce about 27,000 lbs. of filament per year. The quantity of acceptable material would obviously be less due to yield and operability factors which are not known well enough at this time.

Growth in the capacity of the plant to about 60,000 lbs./yr. gross was provided for in the original sizing of gas handling facilities, etc., so that it could be accomplished by one or more of the following steps:

1. Increase filament deposition rate and speed to about 100 or more feet per minute. This would probably require somewhat longer reactors for which head room was planned.
2. Substitution of eight of the new high speed integrated reactors (for which the technology has been largely demonstrated in this program) would give a gross capacity of 36,000 lbs./yr. at 1000 feet per minute, on the same basis as was discussed for the basic plant.
3. Multiple filament high speed reactors were envisioned to permit multiplying the output by a factor of at least 4 or 5. While RF heating of multiple filaments has been demonstrated, the complete development and design trade-offs have yet to be made. It could well be that when this is done, a new larger plant would also be deemed to be more economical than adding this equipment to a pilot plant.

#### C. COSTS OF BORON ON GLASS FILAMENTS

The estimated cost for hydride-type boron on glass filaments is considered to be more sensitive to volume, especially in small amounts/year that are the costs for some other filaments. This is due primarily to the limited production of diborane, the specific sizes and location of production units, and the associated prices for this material. However, based on quantities of diborane in the range of several million pounds per year, and



a filament plant located "across the fence" from the diborane plant, prices of from under \$5 to \$8 per pound are estimated from High Energy Fuel Program production estimates as well as more recent information. (Current diborane costs in small quantities are in the \$90-100/lb. range).

By comparison, the other raw materials (glass and carbon) are almost negligible. GE-177 glass in cane form ready for remelting and drawing of monofilament, for instance, is estimated to cost \$5-7/lb. in 100,000 lb. quantities. A pound of glass would be sufficient to make about 10 pounds of boron filament, so the price of glass per pound of boron would be about 50-70¢ at the million pound per year level (current laboratory produced GE-177 glass is \$25/lb.).

These materials costs plus estimates for labor and depreciation (plant and equipment) indicated that the integrated diborane on glass process should produce filaments for well under \$50 per pound even in single filament reactors and for somewhat less in multiple filament machines.

## APPENDIX A

### PROCESS CHEMICAL ANALYSIS

#### 1. Gas Chromatographic Analytical Procedure

An F&M Scientific Co. Model 810 (Hewlett-Packard Co.) gas chromatograph equipped with a thermal conductivity detection bridge was used to monitor feed, reactor and exhaust gases during the preparation of boron filament by decomposition of diborane. The analytical columns were aluminum tubing, 1/8 O.D x 6 feet long, packed with silanized Hy-Pak; the liquid phase was silicone oil (DC-550). The column was kept at room temperature to minimize decomposition of the intermediate hydrides, and the helium sweep rate was adjusted to the lowest possible rate to permit separation of the diborane and tetraborane peaks, while at the same time achieving the minimum total elution time for each sample. Longer columns failed to pick up pentaborane-11 and were also too slow for rapid sampling.

The gas injection system shown in Figure A-1 consisted of a small manifold to which were attached the calibrated loop (A), a small manometer (B), the injection valve (C), a calibration fixture (D), a nitrogen purge line (E), and an exhaust line (F). A Pirani gauge (G) was used for periodic leak checking. Transfer lines (H) and a sampling valve (J) between the remote sampling point to the injection manifold complete the arrangement. The sampling valve was attached on both conventional mercury electrode and radio frequency heated reactor systems. The latter was not equipped with individual stage analytical sampling points since there were no stage separators as there were in the mercury electrode apparatus. Both systems were fitted with feed and exhaust sampling points. The sampling system for the mercury electrode reactor is shown in Figure A-2. Except for the individual sampling valves, the system was identical for the radio frequency heated reactor.

The chromatograph was calibrated with pure diborane and pentaborane-9 in the range of interest for the actual analysis, i.e. at attenuation

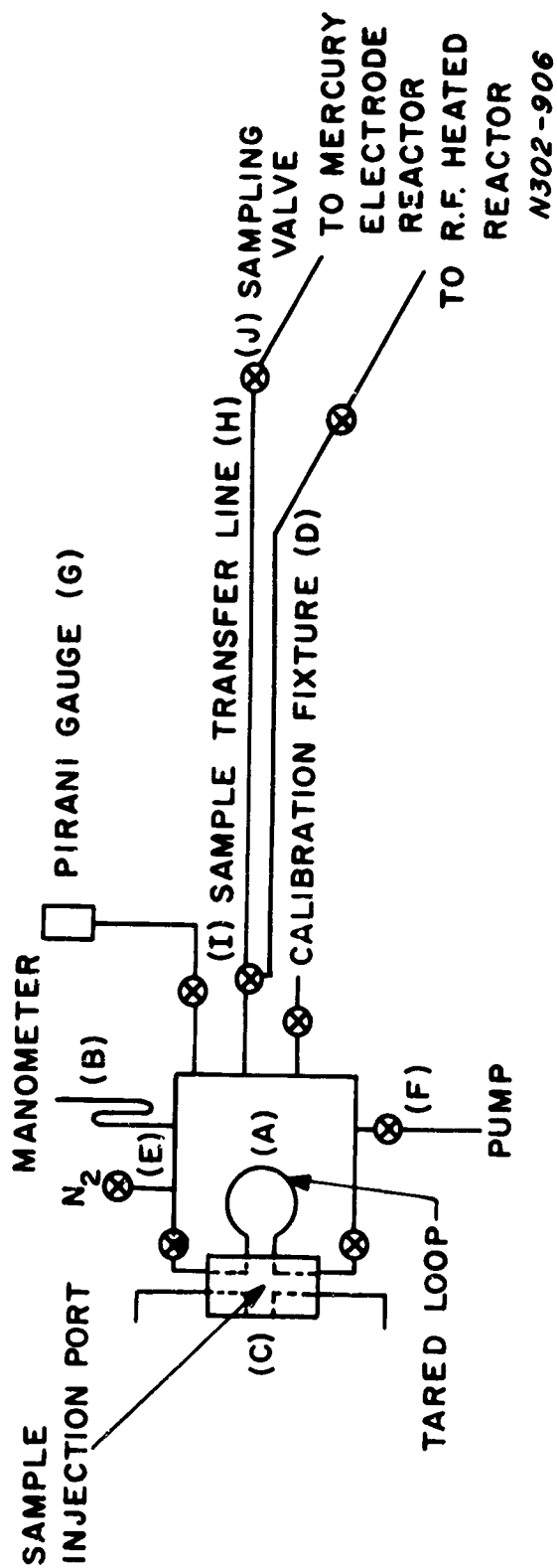
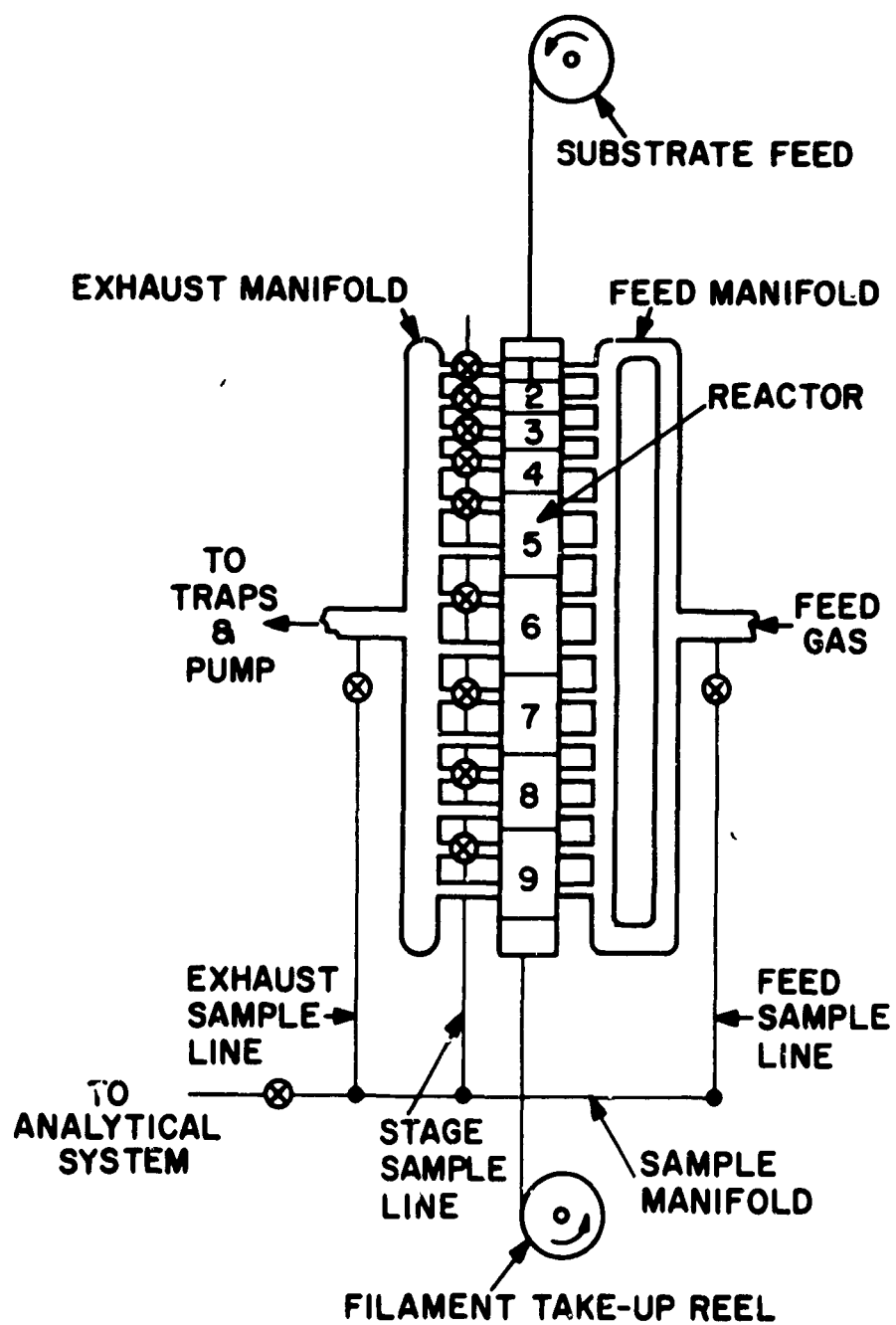


Figure A-1. Chromatograph Sampling System.



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Figure A-2. Schematic of Sampling Points on Prototype Reactor.

settings of 64 and 1 respectively using the peak height values for known amounts of sample. A tetraborane-10 curve was constructed from the pentaborane-9 curve assuming similar heat transfer properties and compensating for the difference in molecular weight. Pentaborane-11 values were obtained from the pentaborane-9 curve. The precision of these last two curves cannot be estimated, but there appeared to be some validity for using this procedure in view of their instability in the pure state.

In sampling at any point in the reactor system, feed, reactor or exhaust, a gas sample was admitted at reactor pressure to the measuring manifold and discarded. This was to reject any stagnant gas on the reactor side of the sampling valve (J). A second sample was then immediately taken, its pressure read on the manometer, and injected into the analytical column. An injection period of thirty seconds was allowed. After injection, the sampling manifold was evacuated for five minutes prior to taking another sample.

Diborane eluted at about 48 seconds,  $B_4H_{10}$  at 75 seconds,  $B_5H_9$  at 150 seconds and  $B_5H_{11}$  at about 200 seconds. Decaborane traces also were seen at about 1000 seconds in true quantities which were too small to be useful. No hydrogen reverse peak was observed. After recording the diborane peak at attenuation setting of 64, the attenuation was changed to maximum sensitivity at 55-60 seconds to obtain separation of the  $B_4H_{10}$  peak. Following elution of the  $B_5H_9$  fraction, the sequence was repeated. Maximum sampling frequency was about one every six minutes. Figure A-3 is a typical chromatogram for an exhaust gas sample of 5 cc.

The procedure was checked to make sure no separation occurred in the long transfer line (H). None was observed, but the line was changed periodically to prevent the possible build-up of solids from causing separation or reaction.

The chromatograph also detected air leaks into the sampling system as well as nitrogen leakage into the reactor from the end caps so that it served a valuable purpose in this respect as well.

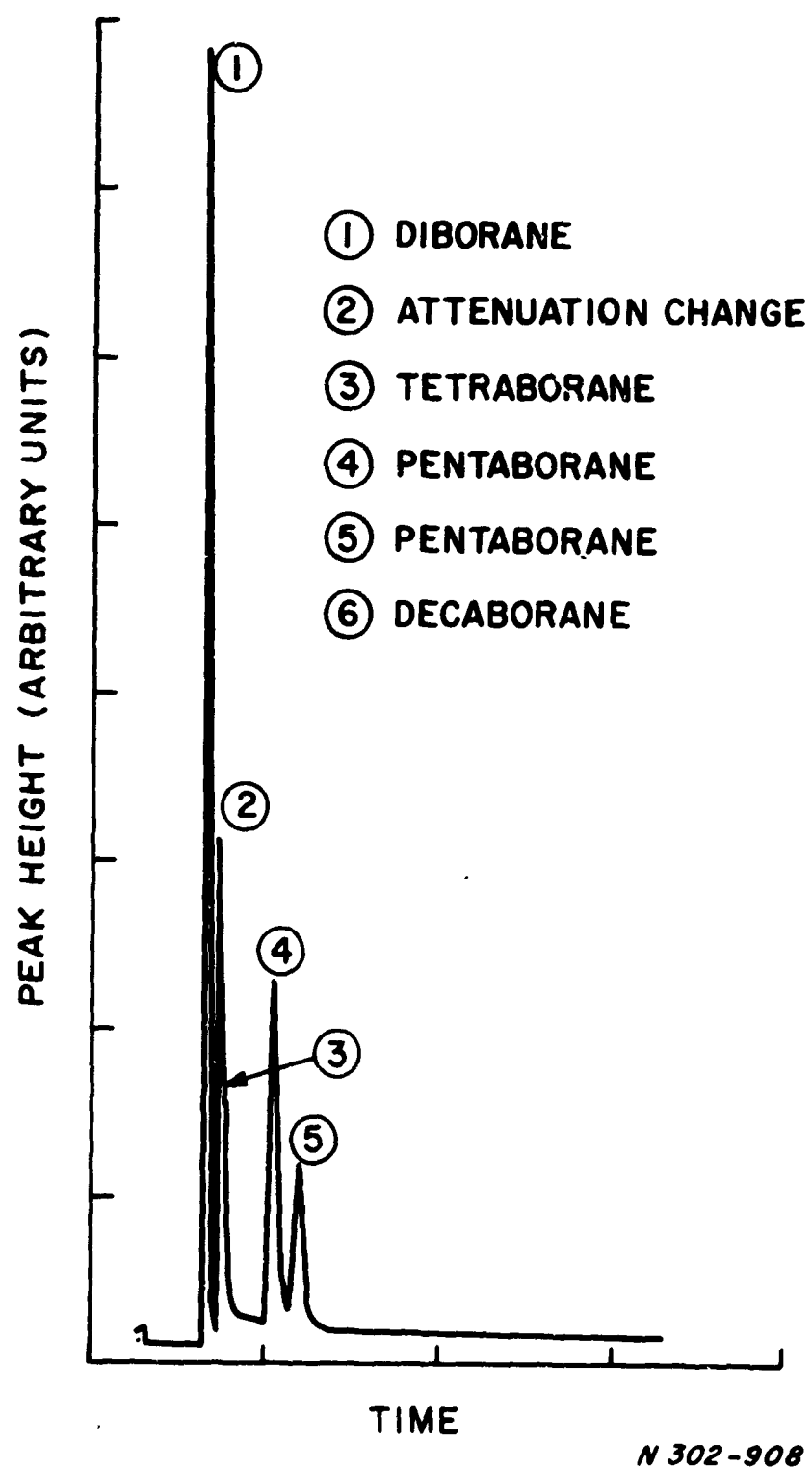


Figure A-3. Typical Chromatograph Trace of External Gas From Reactors.

## 2. Data Reduction

The number of moles of each borane component in the sample was read from the appropriate calibration curve. The total number of moles was then subtracted from the number of moles injected as calculated from the measured pressure, loop temperature and the gas law. The hydrogen content was determined by difference. The largest analytical uncertainty arose from the pressure reading which could be made to  $\pm 0.5$  torr, or about three percent. Larger uncertainties in the total analytical picture were believed to be due to unsteady reactor feed and exhaust conditions. Periodically, helium leakage was caused by deteriorating "O" rings in the sample injection valve. To check column performance, feed specimens were analyzed for thirty minutes prior to applying electrical power to the filament in the reactor. In this way, excess hydrogen was bled off and when a steady diborane content was obtained, it compared well with the calibration curve.

## APPENDIX B

### MATERIAL BALANCE CALCULATION

The purpose of the material balance calculation was to determine the amount of diborane required to prepare a given quantity of boron filament. To do so, it was necessary to use the analytical technique devised and described in Appendix A to assay the feed and exhaust gas for the various gaseous boron components, to account for the boron remaining in the reactor as solid hydrides, and to develop a method for using the assays to place the boron balance on an absolute weight basis. These quantities are shown schematically in Figure 58.

Analysis of the gas streams on a mole percent basis posed no difficulty inasmuch as the borane components were obtained from calibration curves and hydrogen was determined by difference. However, although the amount of diborane fed to the reactor as pure feed was known from mass calibrated flowmeter readings, the gas exhaust left the reactor with a variable composition at a reduced pressure. Furthermore, the exhaust rate from the reactor differed from the feed rate by virtue of the volume changes associated with the decomposition and pyrolysis reactions which occurred with formation of the filament. In order to close a mass balance it was necessary to determine either the volume or velocity of the gas leaving the reactor. A less desirable method in the experimental equipment available was to weigh the diborane before the run and after the run to determine the amount fed, and to weigh the amount of material collected in the cryogenic traps to determine the amount recovered. In one case, this was done to check the validity of the assumption made to determine a mass balance by the analytical method.

In an effort to measure exhaust volume directly, a flowmeter was installed before the cryogenic traps. However, this could not be calibrated directly for gases of different compositions, and it proved also to be insensitive to minor variations in the gas flow. Volumes measured, using calibration curves derived through correcting for pressure and composition

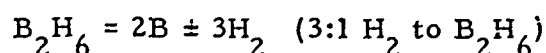


variations, were invariably smaller than volumes fed to the reactor although a volume increase should have been recorded. Consequently, an empirical approach was used which was based on a knowledge of the chemistry of the reactions taking place in the deposition process as well as the composition of the exhaust gas, and the approximate distribution of by-products among the various intermediate species.

The mass balance is expressed as grams of boron fed and recovered per minute (as unreacted diborane, intermediates, filament) and was closed around the lost boron, i.e., boron remaining in the reactor as solid hydrides or lost to the pump. The former could also be determined experimentally in a more suitable apparatus by washing all the lines and the reactor and analyzing volumetrically for boron, which would allow the balance to be closed around the boron lost to the pump. The pertinent components of the mass balance are listed next with the origins of the values used.

1. Feed: Boron, as pure diborane, determined from flowmeter readings calibration by weight.
2. Exhaust Gas: Diborane, tetraborane-10, pentaborane-11, pentaborane-9 from chromatographic calibration curves, computed as equivalent weight of boron. Hydrogen by difference.
3. Boron on Filament: From mass deposited on the length of substrate passing through the reactor per minute, using a density value of  $2.25 \text{ g/cm}^3$  and the initial and final diameters of the filament.
4. Solid Hydrides: By difference as above.
5. Exhaust Gas Components: In the absence of an experimental value, the volume exhausted was estimated by assuming that half of the hydrogen content of the exhaust gas equalled the diborane removed from the gas stream and that the other half represented the volume added over and above the feed volume.

This factor was deduced from the hypothetical reactions



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ABSTRACT

The feasibility of producing CVD Boron filaments using diborane and carbon-coated fused silica (glass) having valuable specific mechanical properties has been previously demonstrated on Contract AF33(615)3268. The purpose of the work reported was to optimize and demonstrate an integrated boron production unit which would incorporate results of the following tests:

- (1) In-line glass monofilament drawing using S-1014 and later GE-177 glass was developed to prepare approximately 1-mil diameter filament at speeds from 50 to 1400 ft. per minute.
- (2) Various coatings and methods of applying them were considered as a means of providing a conductive coating for resistance or RF heatings.
- (3) Numerous dry contact brushes and wheel-type arrangements were considered as a means of eliminating the mercury contacts that are commonly used in present low-speed reactors. These various dry contacts were not nearly as attractive as RF heating which was then developed to the point where it will not only eliminate all direct contacts with the filament during the processing but appears to offer other advantages.
- (4) Process and product improvement studies were primarily aimed at improving the deposition rate, tensile strength, and conversion of diborane to boron filament.
- (5) Automatic Controls were considered to the point where selections can generally be made for usage in the next phase of the program.

Additional related topics including preliminary high-speed reactor design, plant layout, and filament costs are also discussed.

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